ENVIRONMENTAL ASSESSMENT

The History of Contamination in Sediments from the Mersey Estuary

FINAL REPORT 1998

Development of a chronology for the contamination of the Mersey Estuary by Heavy Metals and Organochlorines

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Final Report, 1998
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Executive Summary

In the last decade, large sums of money have been invested by industry and the regulatory authorities on extensive programmes of environmental developments targeted at reducing the impact of pollution on coastal and marine ecosystems. The high level of spending involved has stimulated the need to quantify the resulting environmental improvements. Although changes in some aspects of water quality can be demonstrated from routine monitoring measurements, it is much more difficult to show significant improvements in the impact from persistent pollutants. This arises partly because of the very long time scales involved in the accumulation, degradation and transport of pollutants, in many cases going back before the start of scientifically based environmental monitoring programmes. Suspended sediment particles adsorb pollutants and, where they are laid down in coherent, sequential layers, can provide a record of historical pollution events. If the time sequence of deposition can be determined, then these events can also be dated. This has often been shown for the sediments of large lakes but has proved to be much more difficult in the dynamic estuarine environment.

However, this study has successfully reconstructed a large part of the history of industrial contamination of the Mersey and Ribble Estuaries back to the early part of the last century, many decades before the start of monitoring programmes providing a remarkably detailed picture of very complex changes. The results of the study clearly show the increases in levels of contamination as industry expanded early last century followed by various improvements as this century progressed. Each pollutant has its own idiosyncratic pattern of change with some improvements predating modern environmental concerns whilst other changes seem to relate directly to recent improvements in legislative control. Overall, for the pollutants studied, the results clearly demonstrate the magnitude of improvement that has been achieved in what was a very polluted area. The only major reservation to this story is that despite the wide range of substances covered, many other potentially important pollutants remain to be studied in a similar manner.

A number of technical difficulties have had to be addressed during the study, only some of which have been completely resolved. Others will have to await the deployment of additional resources or more advanced analytical methods. However, the findings of the study suggest that it should be possible to develop a similar detailed picture of changes in contamination for other estuarine areas if the complexities of estuarine processes are taken into account, providing an independent picture of present pollution levels to put alongside contemporary monitoring programmes.

This study examined sediment cores from the Mersey and Ribble Estuaries which had been previously analysed to determine their radionuclide and stable heavy metal contents by Murdock, 1995. New measurements of various organochlorines have been added to the original data and the previous chronology developed by Murdock has been re-examined. Murdock developed a synthetic chronology from a mixture of dates obtained from the pattern of various radionuclides in the cores together with historical records of past change in industrial use of contaminating materials. Murdock derived mathematical relationships to provide an average chronology for each location, although he found that there were some difficulties in reconciling all of the available observations. As a result of this new study, the observations from two sites on the Mersey (Widnes Warth and Ince

marshes) and one site on the Ribble estuary (Banks Marsh) have been rationalised, producing linked chronologies for all three sites, chronologies that are now consistent for heavy metals, radionuclides and organochlorines. The principal dating of the cores relies on 'time signals' derived from changes in radionuclide concentrations together with one based on the appearance of DDT in 1945.

There is a clear record in the sediment of the contamination by each heavy metal (including: Cu, Cr, Hg, Pb, Zn) and organochlorine chemical (including DDT isomers and PCB congeners) studied. The concentration record of each contaminant is idiosyncratic and not synchronous from one to another although most show an increase in concentration from the base of the core followed by a subsequent decrease to the sediment surface. There is a remarkable level of agreement between concentrations of contaminants in cores taken only a few meters apart. These very close similarities have been used as the main argument for developing a system of empirical matching of contamination profiles between adjacent cores, based on lead (stable isotope) concentrations. On this basis, it has been possible to demonstrate that there must have been only minor differences in sedimentation rate between replicate cores collected a few metres apart from one location. Applying corrections for these minor differences in lead concentration improves the fit in patterns of concentration for all of the other contaminant profiles in the replicate cores, reinforcing this view.

The pattern of sedimentation has varied in detail at each location studied. Fortuitously, the sedimentation rates at one site, at Widnes Warth in the upper Mersey Estuary, have been virtually constant through time. Linear regression through the time signals, extrapolated to the base of the core has been determined to be the best available method for dating these cores. No further improvement in fixing the earlier parts of the chronology will be possible without utilising a different technology to fix a time signal lower down the cores. For the purposes of this study just one of these two replicate cores has been assumed to represent linear deposition. The other core is very similar but contains minor discrepancies in sedimentation rate over short periods of time. However, these differences have not been averaged since if they are taken into account, there is a significant improvement in the correlation between the different contamination patterns, the implication being that there is an unexpectedly precise correspondence in concentrations of contaminants between sediment layers of similar age.

The pragmatic conclusion has been reached that sedimentation patterns at each of the other locations studied have been idiosyncratic and have not conformed to any simple mathematical relationship. Accordingly, site specific chronologies have been reconstructed for both Ince and Banks marshes, with intermediate dates interpolated between the main time signals used for dating. Dates in the earliest section of the Banks marsh cores have had to be extrapolated by regression through the two earliest time signals.

The results obtained show significant contamination of the Mersey system with DDT group compounds that appeared very rapidly in the sediments after manufacture of the pesticide had started in Trafford Park, Manchester in 1943.

A similar pattern of appearance applies to the HCH group of compounds after the start of their manufacture at Widnes/Runcorn although only the alpha and beta isomers now remain to any significant extent in the sediments. It has to be assumed that the gamma isomer must be labile in the environment and has been degraded or otherwise lost from the system.

Hexachlorobenzene (HCB) is the only major chlorinated hydrocarbon positively identified in this study which is present in significant amounts early in this century. This unusual pattern of occurrence of HCB in the Mersey can probably be explained by the manufacture of monochlorobenzene as a precursor for the explosive, Picric Acid.

The concentrations of all of the contaminants studied here have radically declined in fine sediments after inputs of pollutants to the system have decreased, although the rates of decline have differed at the various locations.

The results show clearly that there has been a large decline in the contamination of surface sediments by both PCBs and DDT group compounds, although this still leaves the surface sediments contaminated at relatively high levels compared to the wider background. Since new inputs of these materials should now be negligible, this degree of contamination must represent the recycling of buried material.

The results throw some light on the complexity of estuarine processes at local and regional scales. Comparison of the contamination levels of the sediment profiles at Ince Marsh, located in the mid region of the Mersey Estuary and Widnes Warth in the upper Mersey Estuary, shows that during the sedimentation period corresponding to 1940-50, there were concentration differentials between the two locations for many contaminants. This suggests that at that time, there were active sources of these pollutants in the Runcorn/Widnes region. Later, the pattern in concentrations became virtually identical at both sites, suggesting that for these contaminants, concentrations on fine particles within the estuary are now governed mainly by recycling and not contemporary inputs, with overall levels declining as pollutants disperse and degrade.

Features of the contamination profiles at Banks Marsh on the Ribble suggest that dispersal of pollutants from the Mersey region appears to be connected with the accumulation of sedimentary contaminants in the Ribble estuary.

For the majority of contaminants in the Mersey Estuary, a combination of contemporary inputs and the recycling of contaminated sedimentary deposits means that fine particles currently accumulating on saltmarsh areas are still more contaminated than sediments deposited before the industrial revolution. The exception to the last statement is the element Arsenic for which currently deposited sediments are virtually no more contaminated than particles deposited in the 1820s.

Reference:

Murdock, R.N. 1995 The use of Salt Marsh Sediment Cores to Reconstruct Historical Pollution Profiles in the Mersey and Ribble Estuaries, UK. Report to British Nuclear Fuels plc. IERC, University of Liverpool. 62 pp. + apps.

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1. Summary

This study has successfully reconstructed the organochlorine contamination history of the Mersey and Ribble Estuaries from sediment cores which had been collected from the estuaries and had been previously studied to determine their radionuclide and stable heavy metal contents (Murdock, 1995).

This new study has re-examined the chronology developed by Murdock and rationalised the observations from two sites on the Mersey and one site on the Ribble estuary, producing linked chronologies for all three sites which are consistent for heavy metals, radionuclides and organochlorines.

There is a clear record in the sediment of the contamination by each heavy metal and organochlorine chemical studied. The record of each material is idiosyncratic and not synchronous although most show an increase in concentration followed by a decrease to the sediment surface.

The record of contamination had originally been connected by Murdock (1995) to a synthetic chronology derived from a mixture of dates obtained from the concentration of various radionuclides in the cores together with historical records of past industrial changes in the uses of contaminating materials. Murdock used mathematical relationships to provide an average chronology for each location although there were some difficulties in reconciling all of the available observations.

Both studies have shown a remarkable level of agreement between concentrations of contaminants in cores taken only a few meters apart. These very close similarities have been used as the main argument for the empirical matching of contamination profiles between adjacent cores, based on stable lead concentrations.

Using the empirical corrections, it has been possible to demonstrate that there have been minor differences in sedimentation rate between the cores at different times. Corrections for these differences, improve the fit between all of the other contaminant profiles in the replicate cores.

The pragmatic approach has been taken that sedimentation patterns at each of the locations studied have been idiosyncratic and have not conformed with simple mathematical relationships so that site specific chronologies have been reconstructed, with intermediate points interpolated between the time signals used for dating.

Fortuitously, the sedimentation rates at Widnes Warth have been virtually constant through time. Extrapolation through the time-signals using linear regression has then been used as the best available method for dating the bottom sections of the cores. No improvement will be possible without utilising another technology to fix a time signal lower down the cores.

The concentrations on fine particles of all of the contaminants studied here have radically declined after inputs have decreased, although the rates have differed at the various locations.

The results show that for the majority of contaminants, a combination of contemporary inputs and the recycling of sedimentary deposits still results in the contamination of fine particles currently accumulating on saltmarsh areas.

The exception to the last statement is Arsenic for which inputs and recycling are now such that fresh particles are virtually no more contaminated than particles deposited in the 1820s.

The results show clearly that there has been a large decline in the contamination of surface sediments by both PCBs and DDT group compounds, although this still leaves the surface sediments contaminated at relatively high levels compared to the wider background. Since new inputs of these materials should now be negligible, this degree of contamination must represent the recycling of buried material.

The results show that there has been very significant contamination of the Mersey system with DDT group compounds which appeared very rapidly in the sediments after manufacture had started in Trafford Park in 1943.

A similar pattern of appearance applies to the HCH group of compounds after the start of their manufacture at Widnes/Runcorn although only the alpha and beta isomers remain in the sediments.

Hexachlorobenzene is the only major chlorinated hydrocarbon positively identified in this study which is present in significant amounts early in this century. The unusual pattern of occurrence of HCB in the Mersey can probably be explained by the manufacture of monochlorobenzene as a precursor for the explosive, Picric Acid.

Comparison of the contamination levels of the sediments collected at Ince Marsh and Widnes Warth shows that during the lower part of the Ince cores (c. 1940-50), there were concentration differentials for many contaminants between the two locations, indicating that there were sources in Runcorn/Widnes region.

Later, the changes in concentrations became virtually identical at both sites, suggesting that for such contaminants, concentrations on fine particles within the estuary are now governed mainly by recycling and not contemporary inputs with levels declining as pollutants disperse and degrade.

Dispersal of pollutants from the Mersey region appears to be connected with the accumulation of sedimentary contaminants in the Ribble estuary.

2. Introduction

The Mersey Estuary is widely regarded as one of the most polluted estuaries in Europe but in recent times, the extent of pollution from discharges into the river and the Estuary has been greatly reduced as a result of multi-million pound investments by industry and the water companies in the sewerage infrastructure and sewage treatment. It is essential that the results of this investment are monitored and quantified. To achieve this, the history of pollution in the area needs reconstructing.

Current records of metal and radionuclide contamination in the environment seldom pre-date 1960 as a consequence of early technological limitations and the less stringent legislation of those times. In order to find a perspective from which to classify the current status of our estuaries, it is necessary to determine historical levels of contamination and to relate this to what few data exist on environmental discharges prior to the commencement of annual records. In practice, this information may be as little as the dates from which specific industries began working in the area and anecdotal knowledge of the processes and discharges that may have occurred. However, by utilising methods for the dating of sediment cores taken from the estuary, it is possible to reconstruct the pollution history of the estuary from pre-industrial times to the present day, thus extending current knowledge of contamination levels by as much as 100-150 years.

3. Aims and Objectives

The main objective of this investigation was to construct chronologies for the organochlorine pollution which has occurred in the Mersey Estuary utilising sediment cores collected from two stable salt marshes in the estuary. These were to be compared with similar cores collected from the estuary of the River Ribble, some 30 miles to the north. The suite of organochlorines to be studied was to include hydrophobic compounds with similar properties to the Polychlorinated Biphenyls (PCBs) but would include a number of pesticides and industrial chemicals.

Measurements of natural and artificial radionuclides and stable metals had already been completed in the same cores as part of a previous investigation (Murdock, 1995) to prepare dated concentration profiles. Dates derived from patterns of radioisotope deposition were used in conjunction with events in historical time, based on a survey of the industrial history of each of the study areas, namely part of the Mersey Basin (especially Widnes-Warrington-St Helens) and the catchment of the Ribble Estuary.

In the earlier study (Murdock, 1995), discharge records of radionuclides from the British Nuclear Fuels Ltd (BNFL) site at Sellafield, Cumbria had been used in conjunction with a dispersion model which predicts the concentrations of these metals in the dissolved and particulate phases in the Irish Sea for any time period since records began in 1952. Fairly good agreement was obtained between the output of the model and the core measurements although there were a number of remaining discrepancies when the project had been completed.

The specific aims of the project were to:

1. To construct chronologies for the organochlorine pollution which has occurred in the Mersey Estuary utilising sediment cores collected from two stable salt marshes in the estuary.

2. The Mersey cores were to be compared with similar cores collected from the estuary of the River Ribble, some 30 miles to the north.

3. The suite of organochlorines to be studied was to include hydrophobic compounds with similar properties to the Polychlorinated Biphenyls (PCBs) but would also include a number of pesticides and industrial chemicals.

4. A secondary objective of the overall programme was to evaluate the pollution record revealed in the cores against similar estuaries in the UK. and elsewhere.

5. The available data on both radioactive and stable metals which was used for the construction of the chronology of sedimentation was to be re-evaluated in conjunction with the organochlorine data to establish a consolidated chronology for both projects.

4. Background

The Mersey Estuary drains an area of some 5,000 square kilometres including the major conurbations of Liverpool and Manchester. The pollution of the Estuary is a long standing problem with its roots going back to the days of the Industrial Revolution and the birth of the British chemical industry. The Mersey basin continues to be an important area for a wide range of industries with various dock areas retaining their status as major ports. A full description is included in Section 5.

Sediments are generally regarded as the ultimate sink for a wide range of pollutants in the environment, including heavy metals (Lo & Fung, 1992; Chakrapani & Subramanian, 1993), radionuclides (Bonnett *et al.*, 1988; Kelly & Emptage, 1991; Jones & McDonald, 1993) and organic contaminants (Valette-Silver, 1992). In view of this, sediments are often used in assessments of the pollution status of aquatic ecosystems, and as an indicator of human impingement upon them (Valette-Silver, 1992). Much of the previous work in this field has been directed at obtaining chronologies from lake sediments (Appleby *et al.*, 1988 ; Von Gunten *et al.*, 1987 ; Anderson *et al.*, 1987), with specific regard to contamination of the lakes (and thus their sediments) by atmospheric fallout of pollutants. Sediments from areas subject to fluvial transport such as marine, coastal and estuarine systems may not only be an indicator of atmospheric inputs but also of localised pollutant discharges to the aquatic environment (Marcus *et al.*, 1993), and may provide unique localised information on industrial growth and decline through analysis of sediment records.

A comprehensive review of geochronological dating techniques for freshwater and marine environments is given in Valette-Silver (1992).

Pollution assessments using surface sediments are often fraught with difficulties including problems associated with consistent sample site location and composition, resulting in complex correction factors and a need for a high degree of sample replication. This is especially true for estuarine environments where tidal patterns and the unpredictability of accretion-erosion balances induce short- and long-term changes in sediment deposits that cannot always be directly addressed in the design of sampling campaigns. However, where sediments are laid down in sheltered aquatic environments, they become physically stable with time. As a result, they record the concentrations of various environmental pollutants at the time of sediment deposition (French, 1993). Consequently, if a site can be located that has not been subjected to significant physical and/or chemical disturbance, the sediment sequence obtained through sediment coring can provide a chronological record of pollutant concentrations over an extended period of time (Wenning *et al.*, 1994 ; Marcus *et al.*, 1993; Mackenzie & Scott, 1993; Klos & Schoch, 1993; Zwolsman *et al.*, 1993). The factors involved in interpreting data from sediment cores collected from salt marshes are discussed in more detail in Section 6.

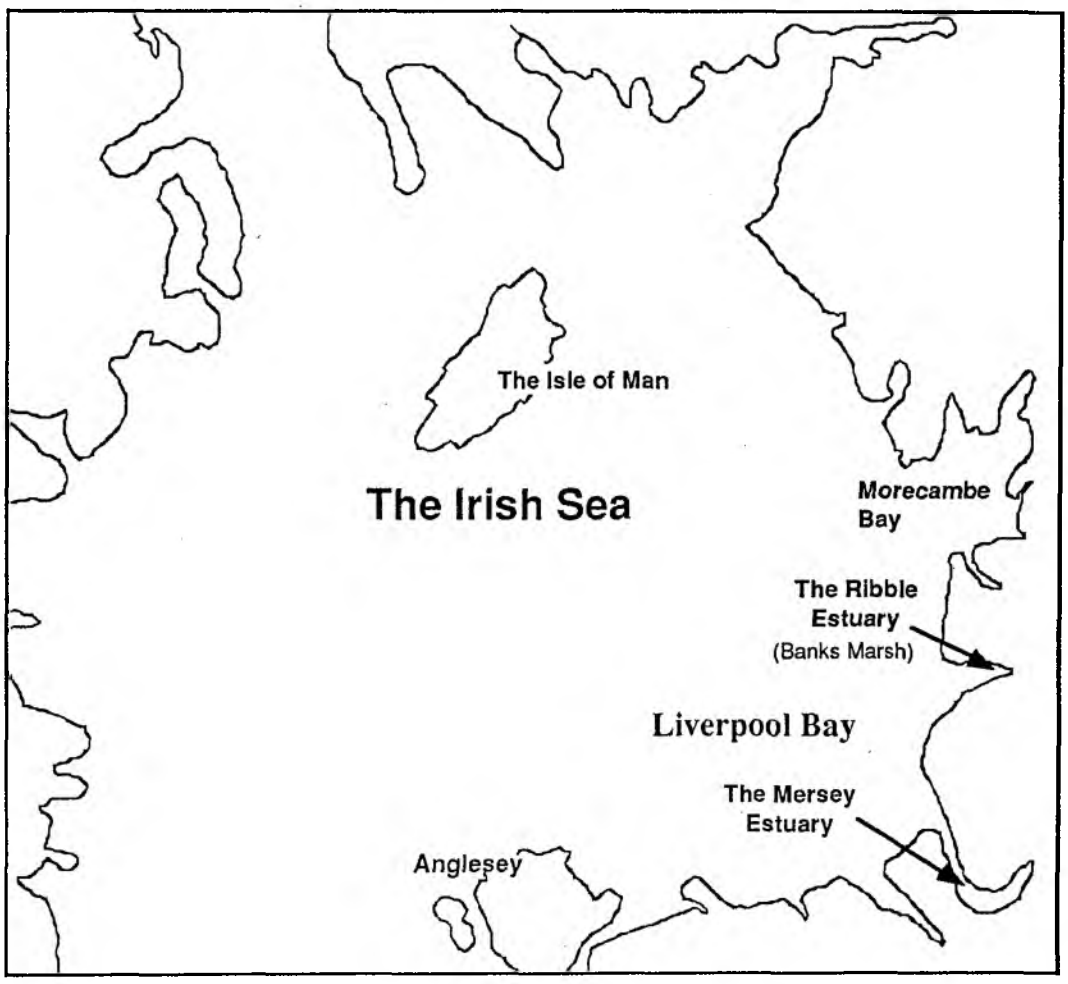

Fig 4-1 Location of the Mersey and Ribble Estuaries

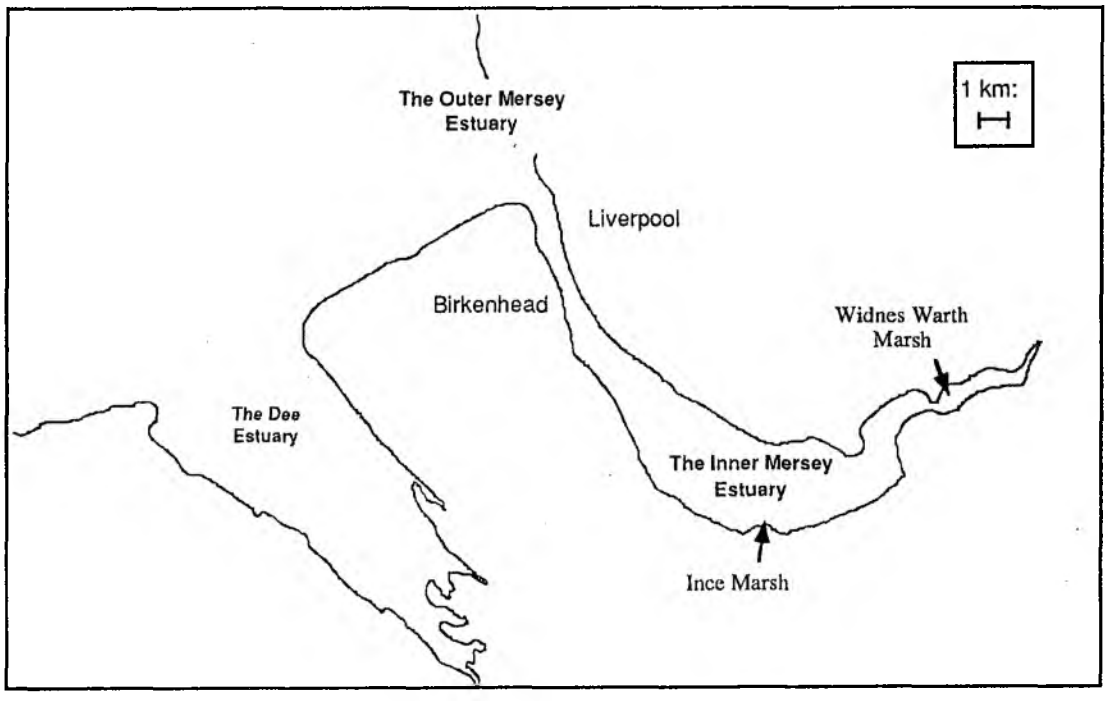

Fig 4-2 Location of the sampling sites on the Mersey Estuary

Salt marshes occur in inter-tidal regions of temperate environments and are flat, poorly drained areas of land subject to periodic flooding by sea water. They are characterised by saline soil and the presence of halophytic vegetation. Important as wildlife habitats and as sources of nutrients for estuaries, salt marshes are also important in coastal defence (Fletcher *et al.*, 1994b). Being elevated above the mean high water mark, they are only subject to total inundation on the highest tides, although some zones are inundated more frequently and where channels dissect the system, upward percolation of water could, in theory at least, occur through the sediment profile.

Salt marshes are typically uniform in surface elevation, varying by as little as 0.3 m over their entire surface area, except where broken by drainage channels or gullies (Jones *et al.*, 1994). Although a number of chronologies have been obtained from open mud banks, it is generally accepted that these environments are less stable than vegetated salt marshes as a result of the relatively high levels of physical disturbance that they are subject to from bioturbation and surface erosion (McCaffrey & Thomson, 1980 ; Chakrapani & Subramanian, 1993 ; Beasley *et al.*, 1986; Fletcher *et al.*, 1994a).

Salt marshes are more protected from physical disturbance than either mud flats or surface estuarine sediments. This is due in part to the low flow velocities that occur during tidal inundation and also through the protection from wind erosion afforded by vegetation between inundation periods. As a result of this stability, salt marshes can provide ideal locations for geochronological dating studies (McCaffrey & Thomson, 1980 ; Valette-Silver, 1992).

The process of marsh accretion occurs *via* the trapping of sediment by vegetation during marine inundation (Oldfield *et al.*, 1993 ; Jones *et al.*, 1994). Typical sediment accumulation rates of established marshes are in the order of 2 - 10 mm y^{-1} (Kelly & Emptage, 1991 ; Jones *et al.*, 1994). The rate of accretion of a salt marsh is believed to decrease with time as the marsh surface is raised relative to the tidal height range and so is inundated less frequently (Allen, 1990). Thus, well established marshes are often found to accumulate sediments at levels approximating to the degree of local sea level rise (Church *et al.*, 1981 ; Vernberg, 1993).

This mechanism favours the deposition of fine sediments (Carson *et al.*, 1988 ; Kelly & Emptage, 1991 ; Bonnett *et al.*, 1988 ; Oldfield *et al.*, 1993), and it is these that typically contain elevated metal and other pollutant concentrations (Chakrapani & Subramanian, 1993 ; Valette-Silver, 1992 ; Oldfield *et al.*, 1993). High specific metal and radionuclide concentrations in salt marsh sediments make these sites significant reservoirs for a number of environmental pollutants (Jones & McDonald, 1993; Kelly & Emptage, 1991). A study by Allen (1990) identified the potential for erosion of salt marshes as an important mechanism in the remobilisation of contaminated sedimentary material. This was suggested for a salt marsh at Ince in the Mersey in relation to increases in surface sediment concentrations of mercury (Taylor, 1986). However, the chemical stability of contaminants bound-up within salt marsh sediments is of great importance in determining the toxicity of any pollutants subsequently released back into the aquatic environment through post-depositional mobility (Rae, 1989; Chakrapani & Subramanian, 1993; Kershaw *et al.*, 1990; Jones & McDonald, 1993). There is currently, little evidence on this available for the study area.

If sediment cores are of sufficient length, metal concentrations in the basal sections of the core will approximate to pre-industrial or background levels (Marcus *et al.*, 1993). Indeed, the historical point at which contamination is measured above pre-industrial levels is of great importance in chronological dating. This is the concept of pollutant 'take-off' dates, the specific historical era during which anthropogenic effects first occurred, These may themselves be used in assigning or verifying dating schemes (French, 1993; Allen, 1990).

4.1 The adsorption of contaminant residues in sediments

It is now accepted that saltmarsh sediments can act as good recorders of pollutant inputs into areas (e.g. Cundy et.al., 1997; Latimer & Quinn, 1996; Zwolsman et.al.; 1996) although a number of difficulties of interpretation of the data can remain (Phillips, 1995).

One underlying assumption in the use of sediment cores to develop pollution chronologies is that the post-depositional mobility of metals and organic compounds is only of minor importance (El-Daoushy, 1986). If significant remobilisation occurs, then the sedimentary records should not be used as the equivalent of historical records of pollution. Thus it is of critical importance to quantify the degree of chemical mobility and to establish the geochemical behaviour of contaminated sediments in studies of this nature.

Sequential leaching experiments, such as those reported in Murdock, (1995) have often been performed on sediments to quantify the extent of sediment diagenesis and post-depositional mobility for stable metal contaminants (Chakrapani & Subramanian, 1993 ; Rae, 1989) and radionuclides (Cook *et al.*, 1984 ; Murdock, 1992). These not only reveal the fraction of sediment-bound contaminant that is freely mobile, readily exchangeable or water soluble, but also give an indication of the dominant geochemical species for each contaminant. This is also important in relation to post-depositional releases of toxic pollutants and their potential re-mobilisation into marine food chains (Kershaw *et al.*, 1990 ; Jones & McDonald, 1993 ; Chakrapani & Subramanian, 1993).

The environmental fate and behaviour of organic pollutants is also ultimately determined by their physicochemical properties and that of the particles on which they become adsorbed. Organic matter has been shown to be the predominant factor controlling the capacity of sediment to bind the hydrophobic chlorinated substances studied here (Karickhoff, 1984). There has been much effort put into developing methods for the 'normalisation' of organic contaminants with respect to some sediment property such as aluminium or organic matter (eg Koelmans et.al., 1997) to reveal the degree of enrichment represented on the fine particles. However, this should not be an issue for this study, since it is known that concentrations of pollutants will be altering through time, whereas the sediment properties have been maintained to be constant by careful selection of the sites sampled. Information on the organic matter is reported below but no normalisation has been applied to the contaminant data reported.

Although, some aspects of the mobility of metals were examined in the associated study (Murdock, 1995), the mobility of organic compounds in these cores has not yet been directly assessed.

Unlike metals, organic pollutants can break down to more simple substances in the environment. However, circumstantial evidence reported here and various studies in the literature (eg. Beurskens et.al., 1993; Kjeller & Rappe, 1995; Wong et.al., 1995; Latimer & Quinn, 1996) lend credence to the suggestion that the stability of many organochlorine compounds in anaerobic sediments must be high.

Bioturbation is one process which if it occurred to a large extent could blur the sedimentary time record although in practice, the effect seems to be relatively small. Ewald et.al. (1997) concluded that bioturbation can increase the sediment to water flux of organic materials but that oligochaete bioturbation in their freshwater microcosm did not alter the profile of one chlorinated biphenyl. Diffusion appeared to be the dominant process governing pollutant dispersion. Schaffner et.al. (1997) showed that there was some effect in an estuarine system, although it altered with season.

4.2 Chronologies represented by sediment cores

The derivation of a time-based sequence of pollutant concentrations from sedimentary records requires the application of one or more sediment dating techniques. These can be based on some physical property such as visible layers of material laid down at different times which can be counted (eg Axelman et al., 1995) or on the measurements of radioactive elements which because radioactive decay is constant, can be used to estimate the time since deposition.

The cores for which results are reported here, were originally taken and analysed in a study funded by BNFL plc investigating the sedimentary history of the estuary in terms of heavy metals and radionuclides (Murdock, 1995). A combination of techniques based principally on radioactive decay had to be employed in that study to obtain a sediment chronology covering cores from the Mersey Estuary at Widnes and Ince and the Ribble Estuary at Banks Marsh. Various problems with the interpretation of the data obtained were noted in the original study by Murdock, so that the data has been re-examined below and interpreted in combination with the organics concentration data produced in this study. As a consequence, fairly full details of the dating methodologies used by Murdock are given below.

4.3 Radiometric Dating

The most commonly used radiometric scheme utilises the atmospheric deposition of ^{210}Pb and its subsequent exponential decay to derive dated profiles. This technique has been applied in lake studies (Appleby *et al.*, 1988) as well as in marine and coastal research (Hendy & Peake, 1996; Axelman et.al., 1995; Lo & Fung, 1992 ; Anderson *et al.*, 1987 ; Von Gunten *et al.*, 1987; Hoshika & Shiozawa, 1984; Church *et al.*, 1981; McCaffrey & Thomson, 1980 ; Goldberg *et al.*, 1979 ; Beurskens et al 1993

^{210}Pb is present in atmospheric fallout as a result of the natural series decay of ^{238}U to the gaseous ^{222}Rn which escapes from its parent matrix into the atmosphere (Robbins, 1978). This short-lived radioisotope (half-life = 3.83d) decays through a number of daughters to ^{210}Pb which is deposited, at an assumed constant rate, to the surface as an aerosol particle. Atmospherically deposited ^{210}Pb is rapidly bound into sediments and as it is buried by successive layers of sediment, it decays with a half-life of 22.3 years (Anderson *et al.*, 1987). However, ^{210}Pb is also present in geological matrices through the decay of ^{238}U inherently present within the matrix itself, such that this 'supported' ^{210}Pb fraction requires subtraction from the total ^{210}Pb content to leave the fraction present from atmospheric deposition alone, known as 'unsupported' ^{210}Pb.

A number of isotopes may be used to estimate supported ^{210}Pb, the most commonly used of which is ^{226}Ra which is quantified through emanation of its daughter ^{222}Rn (Koide et al., 1972). This method has been successfully applied to marine and salt marsh sediments (El-Daoushy, 1986 ; McCaffrey & Thomson, 1980 ; Church et al., 1981 ; Kershaw et al., 1990). More recently, ^{226}Ra has been measured via gamma assay of its daughters ^{214}Bi (Anderson et al., 1987) and ^{214}Pb (Appleby, pers.comm). Following measurement of unsupported ^{210}Pb, a number of models may be applied to the core profile in order to calculate dates (Appleby & Oldfield, 1978 ; Appleby & Oldfield, 1983).

4.4 Non-Radiometric Dating of Sediment cores

Often, a second independent method of core dating is required to validate the chronologies determined through ^{210}Pb measurement (Anderson *et al.*, 1987 ; Von Gunten *et al.*, 1987 ; Abril *et al.*, 1992) or where the ^{210}Pb technique is not successful (El-Daoushy, 1986 ; Beasley *et al.*, 1986). Atmospheric fallout of artificial radionuclides such as ^{137}Cs and $^{239,240}Pu$ arising from atomic weapons testing has been

widely used for this purpose (eg. Simpson *et al.*,, 1976 ; Beasley *et al.*, 1986 ; Von Gunten *et al.*, 1987 ; Anderson *et al.*, 1987). Peak atmospheric fallout of these isotopes occurred on a global scale around 1963, thus providing a useful historical marker.

Artificial radionuclides may also be used to date sediments on a more localised scale. British Nuclear Fuels plc (BNFL) is licensed to discharge a number of radionuclides into the Irish Sea from their nuclear fuel reprocessing plant at Sellafield in Cumbria. Discharges from this site have been recorded since they began in 1952 and provide useful historical information against which radionuclide concentrations in estuarine sediments can be calibrated. A pronounced maximum discharge of ^{137}Cs, ^{241}Am and $^{239,240}Pu$ from Sellafield occurred in the mid 1970's followed by a decrease of two orders of magnitude to present levels (Mackenzie & Scott, 1993).

These effluent discharge maxima are reflected in sub-surface radionuclide concentrations in sediment cores from impacted sites and thus allow an inference of sedimentation rate (Oldfield *et al.*, 1993 ; Kershaw *et al.*, 1990 ; Kelly & Emptage, 1991). Consequently, a series of dated sediment horizons is identifiable. By compiling all this information into a single dating scheme, temporal fluctuations in sedimentation rate may be determined and applied to obtain a chronological record. Cundy & Croudace (1996) have recently reported a similar study on the Solent.

4.5 Movement of pollutants into and out of the study area

A two-dimensional radionuclide dispersion model has been developed by the United Kingdom Atomic Energy Authority at Harwell to predict the movement of dissolved and particle-associated radionuclides in the Irish Sea. The model is described in detail in Howorth and Kirby (1988); a brief summary of the model scope and structure is given below.

The model describes the movement of dissolved and particle-adsorbed radionuclides from their point of discharge into the Irish Sea (the Sellafield pipeline) within an area extending from St Bees head to the north, to Walney Island in the south, and west to the Isle of Man. More recently, this area has been extended north to the Solway Firth and south to the Mersey Estuary.

The interaction between particle-associated and dissolved radionuclide species is controlled by the application of radionuclide specific distribution coefficients (Kd), and it models the transport of dissolved and particulate contaminants by consideration of residual currents and diffusive tidal motions. The model determines the concentration of radionuclides in the dissolved and particulate phases at any point within the grid area, and allows for the deposition of suspended sediments to the sea bed and erosional resuspension of settled sediments into the water column.

The model has been extensively calibrated from field measurements, where possible, and has been validated by comparison with historical records of radionuclide concentrations in different environmental compartments. Predicted future discharge rates have also been run to establish the potential effects of these on the Irish Sea environment.

5. Materials and Methods

5.1 Site Descriptions

5.1.1 The Mersey Estuary

At 8,914 Ha, the Mersey Estuary is one of Britain's largest. It discharges into the Irish Sea and may be divided into **four** discrete regions. The **Upper Estuary,** between Warrington and Runcorn, is a narrow meandering channel around 17 km in length and runs from the emergence of the River Mersey into the estuary at Howley Weir in Warrington to the Widnes or Runcorn Gap, adjacent to the Runcorn Bridge. Immediately west of Widnes, the estuary widens to form the **Inner Estuary,** a large shallow basin 20 km in length and up to 5 km wide in places, with salt marsh on its southern margin. Near Pier Head, the estuary converges to form the **Narrows,** a straight and narrow channel up to 30m deep even at low water, and with fierce tides of up to 6 knots. Seaward of the Narrows, the channel widens into the **Outer Estuary,** an inter-tidal sand and mud bank through which the Crosby and Queens Channels are maintained by dredging. The Outer Estuary connects directly with Liverpool Bay and the Irish Sea (NRA, 1995). There are two main inputs of water to the estuary ; the River Mersey that enters at Howley Weir, and the River Weaver that discharges from the Manchester Ship Canal into the Inner Estuary at the Weaver sluices .

Fine sediments entering or leaving the estuary tend to oscillate with the ebb and flow of tidal movements and may only finally disperse into Liverpool Bay during exceptionally wet weather and large spring tides (Liverpool Bay Study Group, 1975 ; Rice & Putwain, 1987). As a result of this physical process, the estuary may be described as an accretion zone for sediments (Rice & Putwain, 1987). The overall accumulation of sediment in the Mersey Estuary has led to a major problem. The region was once of great importance as a port. In the 18th century the Mersey was navigable as far as Warrington, for shipping of goods to Manchester. As far back as 1760, coal was being transported to Wigan (*via* the Ribble) to the Mersey and Sankey Brook at Warrington (Hardie, 1950). It was therefore essential in past years to ensure that the river channel remained navigable.

The entrapment of large quantities of fine sediments in the Mersey Estuary has also played a significant role in the environmental quality of the estuary. The first serious concern for the pollution status of the estuary came just before the start of the Second World War (WPRL, 1937), at which time a number of remedial measures were suggested. In order to keep pace with the environmental directives of the past 20 years, North West Water Authority, the statutory authority until 1989, launched a broad-based and inter-disciplinary initiative: the *Mersey Clean-up Programme* . This was launched in 1983 with a then committed expenditure of £3.7 billion to the year 2010. Major investment in pollution control continues and further major works are planned (NRA, 1995). The programme aims to provide a number of primary and secondary treatment works in Manchester and Liverpool, to complement the new Sandon Dock facility on the eastern shoreline in Liverpool dockland and thus reduce the discharges of domestic and industrial waste to the estuary.

In 1979, about 2,400 waders, wildfowl and gulls were found dead or dying in the middle reaches of the Mersey Estuary, in circumstances indicative of poisoning. Further mortalities, mainly involving gulls, were noted in the late summer and autumn of 1980. A few birds were reported sick or dead in 1981. Data from an incident report from the (then) North West Water Authority (Head *et al.*, 1980) suggest that these mortalities were caused by tri-alkyl lead compounds. These are thought to have been discharged into the Manchester Ship Canal and from there into the Mersey Estuary to accumulate in the food chain, notably in the invertebrate *Macoma balthica.* (Bull *et al.*, 1983). Though not connected directly to this incident, the general metal enrichment of the Mersey

ecosystem is shown in metal concentrations in sediments. A decade ago, these were found to be elevated above background for a number of metals, including chromium (x 10), copper (x 7), lead (x 4), mercury (x 24) and zinc (x 8) (Taylor, 1986), although subsequent studies have shown that these concentrations are now declining (NRA, 1995).

The largest tidal marshes in the Mersey Estuary are at Ince (SJ 435775) and Stanlow on the south bank of the river adjacent to the Shell Oil Refinery. These marshes, although extensive in size, are young when compared to the more established marshes of the Dee and Ribble Estuaries. Ince Marsh is believed to have formed following completion of the Manchester Ship Canal in 1894, as a result of the enhanced depositional conditions created by the entraining wall of the canal (Buxton, 1978). The marsh at Ince is colonised primarily by the grass, *Puccinellia maritima*, which along with the neighbouring Frodsham Score is used for seasonal grazing of cattle and sheep (Rice & Putwain, 1987).

Apart from the extensive salt marshes on the southern bank of the Inner Estuary, a number of other marshes are present along the north bank of the river in the Upper Estuary. The most significant of these are located at Widnes Warth between the river and the St. Helens Canal, and at Cuerdley Marsh which runs parallel to the canal to Penketh near Warrington.

Widnes Warth (SJ 52638492) is a well established salt marsh and is evident in approximately its present form on the map by Greenwood dated 1819 (Buxton, 1978). In contrast to the marsh at Ince, which is probably less than 100 years in age, Widnes Warth may be as old as 250 years and may even pre-date the construction of the St. Helens Canal in 1757.

5.1.2 The Ribble Estuary

The River Ribble emerges into the Ribble Estuary a short distance west of Preston as a narrow channel around 100 m wide. In this region there are a number of well established salt marshes; Clifton, Lea, Hutton and Longton Marshes. The most extensive of these are the latter two which are at the confluence of the River Douglas with the Ribble.

In the upper estuary at the mouth of the Douglas there is much evidence of salt marsh reclamation. Land reclamation in this area began largely in 1860 and was conducted more extensively in the period 1880-1890, with further land being reclaimed for agricultural purposes, into the late 20th century.

Below the River Douglas the channel widens to around 200 m, and is surrounded on both sides by sand and mud banks. The salt marsh known as Hesketh Out Marsh is a short distance below the Douglas on the south bank of the river, and has also been extensively reclaimed. Downstream of this marsh, the channel widens substantially into the outer estuary. The south bank of the river at this point consists of a very significant area of salt marsh known as Banks or Ribble Marsh. This runs for nearly 5 km from Hesketh by the Douglas to Crossens Marsh a short distance north of Southport, at the very mouth of the estuary.

Banks Marsh (SD 38382272) is not only expansive in width, but also extends 2km out into the estuary so that, in places, the estuary itself is not visible from the back marsh. Banks Marsh was chosen for this project as an outer estuary site to complement the Inner Estuary site of the Mersey system at Ince, and the upper estuary site at Widnes.

A large area of land was reclaimed close to the present location of Banks Marsh in the late 19th century. It is believed that the present salt marsh developed from the increased

sedimentation caused by construction of the retaining wall during reclamation. This would date the marsh as being a little over 100 years old, and would correspond to a very significant rate of lateral growth to produce the current marsh size.

5.2 Sampling

Exploratory sediment cores were taken in June and July, 1992 from a number of sites across the width of marshes in the Mersey and Ribble Estuaries. These samples were taken to determine the feasibility of using the sites for chronological studies, and also to quantify any possible differences in sedimentation rate across the marsh surface. A noticeable decline in sedimentation rate from the front to the back of each marsh was observed through the analysis of sub-surface radionuclide peaks, such that the length of the historical record contained within a fixed core length increased from the front to the back of the marsh. The most suitable sites were identified as those as near to the back of each marsh as was physically possible to sample, with the length of core required to provide the full historical period from pre-industrial times being estimated at no more than 1 m for the sites at Banks and Widnes.

Three sediment cores were removed from each site in November, 1992 using a petrol-driven vibro-corer one metre in length and of internal diameter 100 mm. The cores were collected in a line perpendicular to the marsh edge at intervals of 3-4 m. After driving the coring tube into the marsh deposits, the cores were extruded by a winch system before being cut *in situ* into lengths of 30 cm and stored in sealed polythene bags. The coring tube was rinsed between collection of cores in order to avoid cross contamination from one site to another. Samples were then taken to the laboratory where they were stored in a cold room at 4°C prior to preparation for analysis.

The cores were sectioned laterally at 3 cm intervals within 24 hours of collection, and the central core of each slice was then excised using an 8 cm internal diameter, stainless steel cutting ring. The outer edge of sediment was discarded to eliminate the possibility of including material from other levels through sediment smearing during sampling. The sediments were then loosely aggregated to aid drying and subsequent preparation, air-dried at 20°C and passed through a 2 mm mesh sieve to remove over-sized particles and vegetation.

The sediments were subsequently stored at room temperature in screw-top, glass jars.

5.3 Methods for Radiometric Dating

^{241}Am and ^{137}Cs concentrations were determined on an n-type coaxial HPGe gamma spectrometer (resolution 1.87 keV, relative efficiency 29.4 %) to a fixed planar depth of 10 mm. Radioactive counts were routed through conventional electronics to a multi-channel analyser where nuclide peak details were recorded. Typical count times, as detector live-time, ranged from 6000 to 85,000 seconds (i.e. between 2 and 24 hours).

Radionuclide spectra were analysed using the application OMNIGAM, which uses detector calibration information and user-defined nuclide libraries to determine the activities of specified nuclides. In practice, only the nuclides ^{241}Am and ^{137}Cs were of interest in the context of this project, although a number of other radionuclides were quantified automatically during spectral analysis.

Efficiency calibration of the detector was achieved using standards prepared in the same geometry as the core samples, having been spiked with a known concentration of a mixed gamma nuclide solution traceable to the National Physical Laboratory. Energy calibrations were performed as required using a high activity mixed gamma-emitting standard in Marinelli beaker geometry. Calibrations used the low energy peak of ^{241}Am at 59.54 keV and the high energy peak of ^{60}Co at 1332.5 keV.

^{238}Pu, $^{239,240}Pu$ and a small number of the total ^{241}Am measurements were made by alpha spectrometry *via* a radiochemical procedure involving sample digestion in aqua regia followed by a number of precipitation and ion exchange steps to isolate individual actinide elements. A full description of this method is given elsewhere (Murdock, 1992). The chemical yield for each element was obtained by the use of internal spikes of known concentrations of ^{243}Am and ^{236}Pu tracer solutions, neither of which was naturally present within sediments. Chemical recoveries measured in this way were typically in the range of 76 to 87% for plutonium isotopes and 50 to 55% for americium. The yield tracers used in this procedure are implicitly traceable to AEA Harwell Laboratories.

Radiometric dating of the sediment cores was performed *via* the analysis of ^{210}Pb and ^{214}Pb on a low background well-type HPGe gamma spectrometer. Samples were sealed with wax to prevent the escape of radon gas and left to equilibrate for a period of at least three weeks. The concentration of ^{214}Pb in the sediment is an indicator of the supported ^{210}Pb content of the sediment, such that the difference between measured ^{210}Pb and ^{214}Pb is the unsupported ^{210}Pb used for calculation of geochronology. The procedure used to obtain the dated profiles requires the use of either of two models which are described elsewhere (Appleby & Oldfield, 1978 ; Appleby & Oldfield, 1983).

The dates derived from radiometric analysis of lead isotopes were to be compared with a number of other historical markers, such as the profiles of ^{137}Cs and the actinides, and the 'take-off' dates of some of the heavy metals. Sedimentation rates obtained using historical markers were used to derive an independent dating method for the profiles, which is presented in the next section, and used to validate the dates from radiometric assays.

5.4 Heavy metal Analysis

Copper, lead, zinc and arsenic determinations were made by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) following a sediment digestion in nitric acid and hydrogen peroxide to a final solution of 40% nitric acid. Sediments for mercury and chromium assay were first digested in aqua regia and then measured by flameless and nitrous oxide flame atomic absorption spectrophotometry, respectively.

Sediments were digested in batches of 32, including two reagent blanks and certified sediment reference materials from Buffalo River (National Bureau of Standards : SRM2704) and the Scheldt Estuary (Community Bureau of Reference : CRM277). The mean chemical yields for each metal analysed were as follows : arsenic (96%), chromium (86% acid soluble), copper (92%), lead (88%), mercury (100%) and zinc (95%).

The procedure used for sequential extraction of sediments was based on McLaren & Crawford (1973) as modified by Iu *et al.* (1981) and is described in detail elsewhere (Murdock, 1992). Briefly, 0.5 g of air-dried sediment was shaken successively with a number of reagents (Table 1) which are hierarchical in strength so as to remove the exchangeable and water soluble fraction first, followed, in turn, by the specifically adsorbed, organically bound and the oxide or hydroxide bound fractions. This leaves the resistant or residual, concentrated acid-extractable fraction present on the sediment. Glass centrifuge tubes were used in the extraction of mercury from sediments to prevent losses of this metal on contact with polythene surfaces; for the other metals, polythene centrifuge tubes were adequate.

5.5 Organochlorine Analysis

General Analytical Protocols used for organochlorine analysis are outlined in Appendix 1

5.5.1 PCB analysis

Detailed analytical protocols are given in Appendix 1. Sediments have been extracted by solvent reflux. Sediments were dried and sieved before analysis. Interference by sulphur was removed by refluxing with bright copper turnings. Extracts were cleaned-up on Florisil and silica chromatography columns. No particular analytical difficulties have been encountered for this group of compounds.

In this project we were concerned with obtaining estimates of:

1 Overall levels of PCB contamination
2 Concentrations of specific, identified, individual congeners to relate to toxicity and other factors

This was achieved by:

1. Calibrating some measurements against a simple mixture of seven congeners (ICES7) - providing very precise, unambiguous estimates of individual concentration to provide data for direct comparison with many recent studies reporting data for these 'standard' congeners. Designation: Σ**ICES7** Units: $\mu g\ kg^{-1}$
2. Calibrating some measurements directly against a mixture of Arochlor 1254 providing data for comparison with a wide range of (generally older) literature values of 'PCB concentration'. Designation: ΣPCB_{A1254} Units: $\mu g\ kg^{-1}$
3. Calibrating some measurements directly against a mixture of Arochlors 1242, 1254 & 1260 - providing data for comparison with a wide range of (generally older) literature values of 'PCB concentration'. Designation: $\Sigma PCB_{1:1:1}$ Units: $\mu g\ kg^{-1}$

In establishing the general principles reported here, there is enough similarity between the different measures that most consideration has been given to ΣICES7 as a surrogate for 'Total' PCB.

5.6 Sediment characterisation

Loss on ignition tests to quantify the organic content of each core section were performed at a temperature of 550°C for 4 hours (Allen, 1989). The silt and clay content of each sediment sample was determined by laser diffraction in order to investigate the variation of particle size with sediment depth, and to use the results of the study to assign correction, or normalisation, factors to concentrations if significant (Allen, 1989).

6. Discussion of Methods used in the Dating of Sediment Cores

6.1 Radiometric Dating

This study has been primarily based on the use of radionuclides derived from the reprocessing of irradiated nuclear fuel at Sellafield, Cumbria. The discharges of radionuclides started around the end of World War II and the combination of nuclides has changed over the years for operational reasons. Thus changes in concentrations of these nuclides in sequences of maritime and estuarine sediments can be related back to specific periods of time backwards to around 1950.

However, the period of time 70-80 years prior to the commencement of discharges from Sellafield needs to be included within the study to elucidate the early pollution history of the estuaries. Another methodology is needed for this using radionuclides with a longer history in the environment. It was hoped that the naturally produced isotope of lead ^{210}Pb could be used for this purpose but sensitive enough measuring techniques were not available. This meant that samples in the earlier parts of the cores could not be directly dated either by using the ^{210}Pb model nor by dates derived from Sellafield radionuclides.

Within the incerasing amount of literature on the subject, the radiodating of lakes has been basically dependent on bomb material and ^{210}Pb, that of marine cores on the labeling provided by Sellafield isotopes.

6.1.1 Unsupported ^{210}Pb measurement

Appropriate samples were analysed for a range of radionuclides from each estuary site using the procedure described in the previous section. A number of samples from each of these cores were analysed for total ^{210}Pb and ^{214}Pb *via* gamma spectrometry, and the resultant calculation of unsupported ^{210}Pb was then made.

Unfortunately, the methodology was unsuccessful in practice, since unsupported ^{210}Pb concentrations were too low to successfully date the cores over the full length of the cores.

A limited number of researchers have previously used this methodology to date surface sediment cores from estuaries and coastal environments (eg. Hoshika & Shiozawa, 1984 ; Hoshika *et al.*, 1988), but they have tended to measure unsupported ^{210}Pb *via* radiochemical separation and alpha spectrometry as described in the previous section. However, although the limits of detection for ^{210}Pb are lower for alpha - than for gamma spectrometry, it is still possible that even this method would not enable dating of the sediments for the whole 80 year timespan of interest in these saltmarsh cores. Past successful applications of the ^{210}Pb model have relied on the relatively low sedimentation rates that occur in many lakes and deep ocean sites (Appleby *et al.*, 1988 ; Von Gunten *et al.*, 1987; Anderson *et al.*, 1987) but the much higher deposition rates in saltmarshes dilute the limited supply of ^{210}Pb below that which can be reliably quantitated using available technology.

Typical surface concentrations of unsupported ^{210}Pb in the cores were in the range of 23-39 Bq/kg dry weight, approximately 5-10 times lower than equivalent values reported for lake sediments (Appleby *et al.*, 1988). For one core from Banks Marsh, the concentration of unsupported ^{210}Pb was found to be less than the detection limit at a depth of only 10.5 cm and as a consequence could not even be used to date the top 10 cm of the 100 cm sediment cores. At these concentrations, even assuming there were no

aberrations in the profiles, radiometric dating *via* ^{210}Pb could only be applied to recent (post-1950) sediments, the same period for which good data could be obtained for Sellafield-derived radionuclide concentrations.

Current sedimentation rates for salt marsh environments examined in this study are believed to be in the order of 8 mm yr $^{-1}$, compared with typical values of 1-2 mm yr $^{-1}$ found in most lake environments. Whilst sedimentation rates in salt marsh ecosystems vary considerably within an estuary, as evidenced by the values of 11-22 mm yr $^{-1}$ obtained for the salt marshes, and 3.5-25 mm yr $^{-1}$ for accreting mud flats in the outer Thames Estuary and the eastern coastline of Britain (Fletcher *et al.*, 1994b), the estimates for the Mersey and Ribble Estuaries are consistent with the values of 9-13 mm yr $^{-1}$ for the Scheldt Estuary in the Netherlands (Zwolsman *et al.*, 1993) and upstream locations in the Lower Passaic River, New Jersey (4-6mm yr $^{-1}$; Wenning *et al.*, 1994).

The sediment cores used in this study, were originally collected from carefully chosen locations to minimise the impact of high sedimentation rates on ^{210}Pb concentrations, with cores being sampled from the back edges of the marshes where sedimentation rates are usually lower than sites at the front of the marsh. Even so, it would appear that the accumulation of sediment at the study sites is still too fast to for successful use of radiometric ^{210}Pb dating.

6.1.2 Measurement of Actinides etc.

These were eventually used in the development of the final dating scheme.

6.2 Variation in the Environment

Saltmarshes are very variable environments and it has proved to be very much more difficult to develop comprehensive pollutant chronologies in estuarine sediments than sediments from lakes. This was recognised at the outset so that most analytical measurements have been repeated on duplicate cores taken from locations separated by only a few meters distance. Complete duplication has not been possible for all organochlorine analyses because of limitations on cost. However, the very high degree of repeatability across a very wide range of analytical measurements suggest that this was justifiable.

One major determinant of pollutant behaviour is the nature and size of the associated sediment grains. Much effort has been put into normalisation methods to account for this variation (eg Jones & Franklin, 1997). However, in this study, no normalisation has been applied. This is justified by the specialised circumstances applicable to this study (it is NOT implied that there is no need to normalise in other circumstances). Specifically, the cores are particularly uniform in composition, having been collected from stable saltmarsh sites with long histories of stability. All of the cores were basically comprised of the very fine mud particles which can only settle when the water is very slow moving. Such particles are normally organic rich and as such attract metals and hydrophobic organic compounds.

The sediment cores were certainly not uniform in organic composition with all cores showing an increase in organic matter to the surface (see Figure 6-1 to Figure 6-3). The two Mersey sites cover the same range of values in the same physical depth although they represent very different periods of time (Figure 6-2). The Banks Marsh cores show a similar pattern of increase to the surface (Figure 6-3) but are consistently slightly lower in organic matter. This might account for some of the difference in pollutant concentrations between the two estuaries, tending to make Ribble concentrations lower than the Mersey.

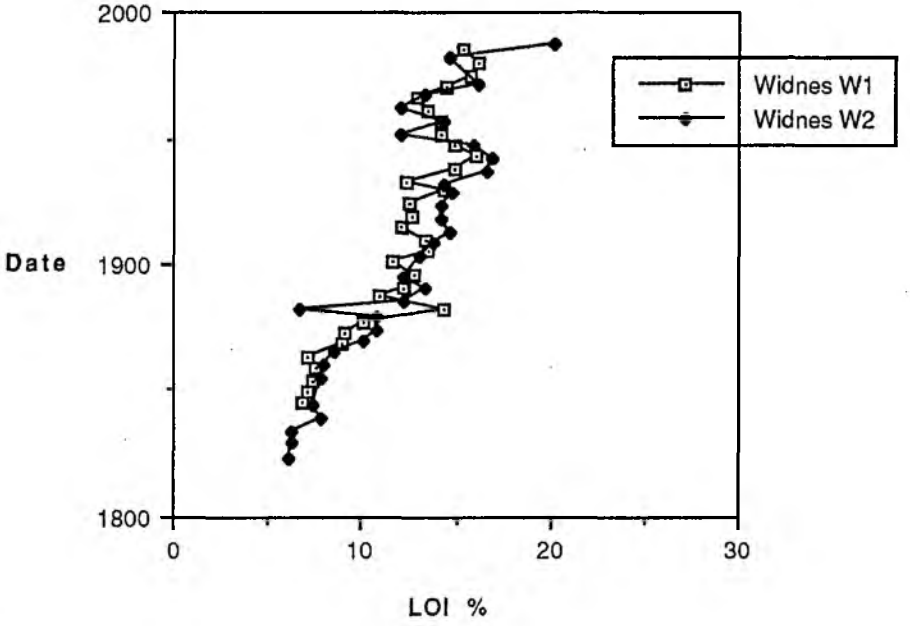

Figure 6-1 Loss on ignition (LOI) in cores from Widnes Warth

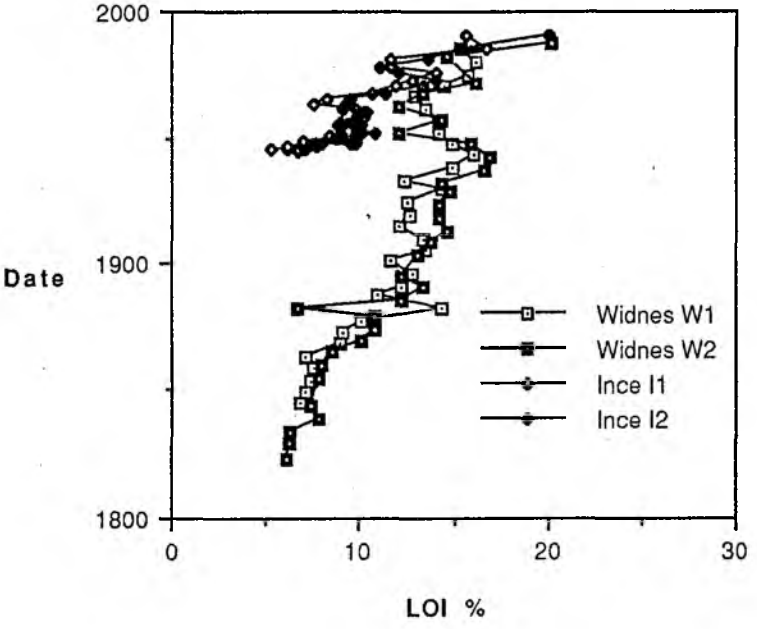

Figure 6-2 Comparison of Loss on ignition (LOI) at Widnes Warth and Ince Marshes

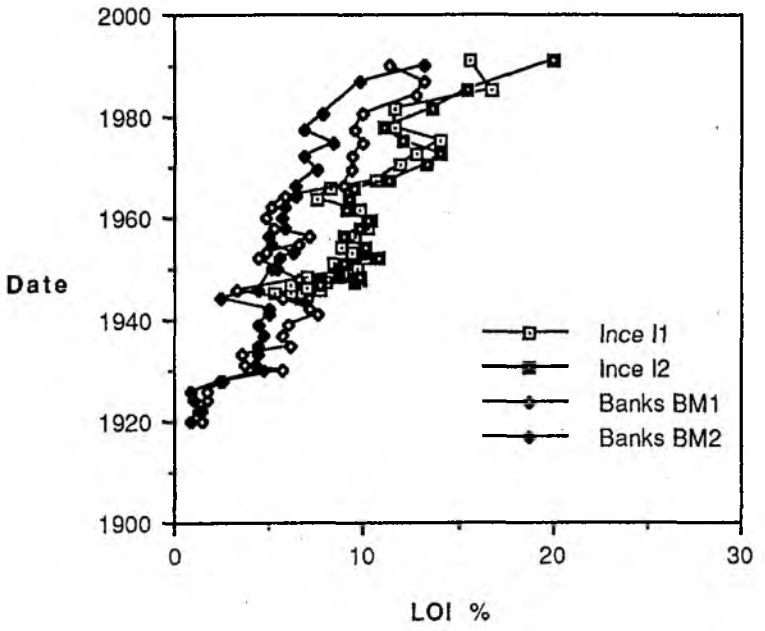

Figure 6-3 **Comparison of Loss on ignition (LOI) at Ince Marsh, Mersey Estuary and Banks Marsh, Ribble Estuary**

6.3 Re-appraisal of the core dating scheme used by Murdock (1995)

As explained in the previous section, there are various limitations with the dating of sediment cores from their contained radionuclides, although the available data was considered to be sufficient to enable a good history of the metal contamination of the Mersey Estuary to be constructed (Murdock, 1995). The contamination history was reconstructed mainly based on averaging the concentration results obtained from two cores from Widnes Warth Marsh (Cores W1 & W2) and the chronology relied heavily on using dates obtained from the industrial history of the area. Although, there were similarities in patterns of contamination with cores obtained from Ince Marsh, it was not possible to reconstruct as good a picture of historical changes for the cores at Ince. These latter cores were taken from an environment where deposition rates of sediment were much greater, a factor which it was concluded was influencing the results. A similar historical pattern of contamination was also observed for Banks Marsh on the Ribble, although much less was known about the industrial history of the area and there were fewer obvious signals to attribute dates to.

When the results of the present study became available for the organochlorines in the original cores studied by Murdock, it was clear that there was also a clear pattern in the contamination profile of organochlorines in the core but that it was difficult to reconcile all of the new features with the previously observed metals profiles.

Thus, it was decided that for the purpose of re-constructing the organic chemical history of the estuary, there needed to be a complete re-appraisal of the dating scheme developed during the earlier study. The specific purpose of the re-appraisal was to determine dates of relevance to the reconstruction of the organochlorine history of the Mersey going back some fifty years although some of the findings have proved to have a wider significance.

6.3.1 Absolute dating vs. Relative dating

Dating schemes used in the literature vary - there seems to be no doubt amongst workers that there is a general relationship of time with increasing depth down a sediment profile but there are many potential pitfalls to attributing absolute date values to particular horizons.

The presence of the artificial radionuclides and the pesticide DDT in the sediment cores studied here gives very clear 'time signals' because the contaminants have a known history of production and are not present in the sediments below certain depths, presumably because these correspond to periods prior to production. These signals, in combination with the clear pattern of contamination observed for the stable heavy metals demonstrate that there is a record of environmental contamination over a long period of time which could be reconstructed if the time signal itself could be determined. Despite the obvious information contained in the record, the interpretation of the contaminant patterns depends on certain assumptions about the behaviour of chemicals in sediments which because of the scarcity of accurate information will limit confidence in the picture built up. However, it is now possible to build-up a self-consistent picture of the contamination history of the Mersey Estuary based on a relative chronology which is fixed to a small number of absolute dates. In future, it is to be hoped that improvements in analytical methodologies will increase the number of absolute dates available to link to the relative chronology.

Murdock (1995) found that a simple, linear model of deposition fitted quite well with his observations at Widnes Warth although most of the fixed points used to determine this were in the upper layers of the cores. He came to the conclusion that working to an accuracy of ±5 years, a linear model was adequate for his purposes. Despite this, a final

dating scheme was used in the preparation of the 1995 report containing a dating scheme which was curvilinear. This was necessary to include the dates, in the lower parts of the cores derived from documentary sources.

The dates provided by the specific time signals (see Table 1) determined in this study coincide in the case of one of the Widnes cores (Core W1) with a simple model of linear deposition. However, if the detail in the patterns of contaminant concentration are compared (see Figure 6-4), it is apparent that there are some small discrepancies between the replicate cores and that the second core (Core W2) does not contain the same clear evidence of linear deposition during the period for which there is specific dating information. If two cores collected from such similar locations can vary in the manner described, it is apparent that either simple linear models should be applied with extreme caution or that the analytical methods are producing results with insufficient accuracy and precision to develop a very clear picture of historical events. For reasons which are developed later in this discussion, it is suggested that the latter possibility of insufficient accuracy and precision should be ruled out. This leaves the conclusion that a new understanding needs to be developed to explain all of the observations.

It was decided that for the purposes of re-appraisal, the emphasis would be put onto dates for which there is analytically based evidence, since the documentary evidence provides less clear-cut signals. In addition, there is not enough information available to understand the lag-times which would be involved before clear sedimentary signals would follow changes in industrial practice.

6.3.2 The Linear Deposition model

Murdock (1995) used a combination of methods to date the cores. The major limitation of the study was that dates based on radionuclides are only available back to approximately 1950. Beyond that, Murdock had to use 'historical evidence' derived from examination of various documentary sources of changes in the industrial usage of materials by Merseyside Industry. One problem in using these sources to develop a chronology is the subjective nature of much of the data which are available. The starting point of this re-examination was to use the unambiguous dates available from features of the radionuclide profiles together with one derived from the organochlorine profile (the introduction of DDT) for which there is exceptionally strong evidence of the likelihood of a very clear time-signal.

If sediment was deposited in such a simple, linear manner, it would be very convenient for investigators, but, it is recognised that the appearance of linearity may be purely fortuitous since, unlike for lakes, there are no *a priori* reasons to assume that sedimentation is likely to follow any simple model through time. The vagaries of the physical processes operating in estuaries are likely to cause very significant alterations in deposition at any geographical point through the length of time over which sediment cores accumulate. There are no reasons why alterations could not operate on timescales of one year or less. It was for these reasons that the sediment cores analysed in this project were originally collected from sites with an obvious, long history of physical stability to increase the likelihood of the complete history of the contamination of the Mersey being contained within them. Again, it is recognised that this may make them special cases and it is not being argued that all of the marsh areas within an estuary would contain the same detailed, unbroken record of contamination through time.

6.3.3 Time Signals

A wide range of dating methods have been considered during the course of this and related investigations with the search being conducted for specific features of the cores which could be attributed to certain precise historical times. These have been mainly based on the known history of dispersal of various radionuclides but which could not

include one of the most useful (^{210}Pb) because of detection limitations (see section 5.3 for details of the methods). Such methods are widely accepted as producing reliable, authenticated dates when properly applied. There are five of these authenticated 'Time Signals' (see Table 1) which can be included in this study, which is one more than Murdock (1995) had available. (This is the appearance of DDT, explained below).

At Widnes Warth, the Time Signals happen to fit very closely to the 'linear' deposition model of sediment on the salt marsh, although this was not the case elsewhere. The history of the site at Widnes Warth and the close fit of the available data has been used as evidence to support the hypothesis that sediment deposition there has been basically linear through time. This has provided a starting point for further consideration. The detailed case for dating was then examined for each set of cores in turn

The regressions through the authenticated Time Signals are similar and suggest that the sequence of sediments in the two cores starts between 1820 and 1840 (see Figure 6-4). These dates are slightly earlier than those suggested in Murdock (1995) where it was assumed that the take-off date for the metals in the Mersey was approximately 1890 based on documentary evidence. However, these new dates do not really conflict with the overall picture put forward by Murdock because of the relatively wide uncertainties which he proposed.

Thus, the differences in dating between two cores collected very close to each other appear to be comparatively minor when the lines are extrapolated back to the base of the core, although the differences are sufficient to blend together the patterns of change recorded in each core. Thus, it is this author's opinion that interpretation of the core data can now be improved by using all of the information which is available and avoiding reliance on documentary evidence for general increases in metals use which can only be very approximate. This is completed in Section 6.4 to Section 6.6 for the three sampling locations.

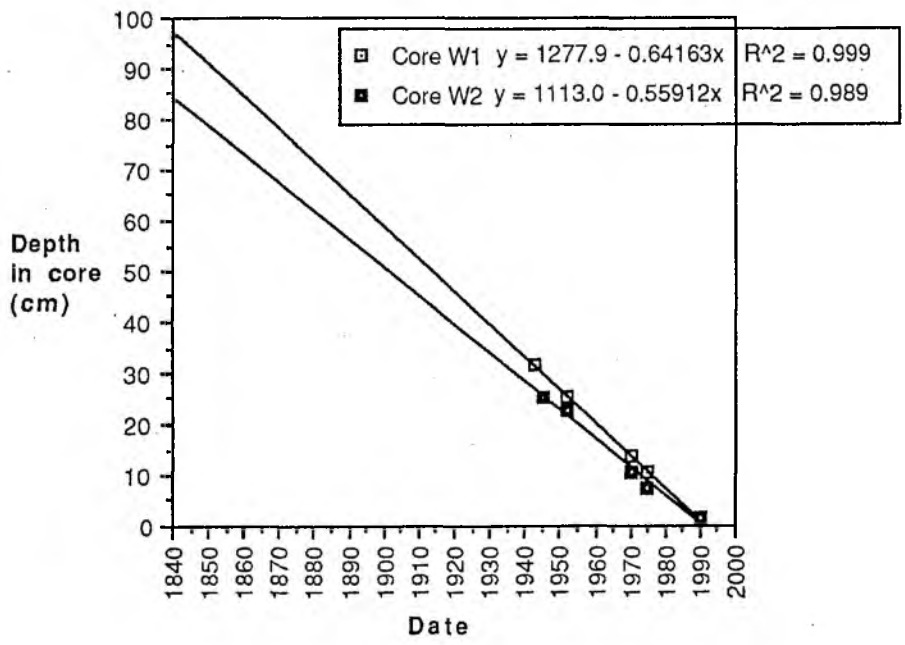

Figure 6-4 **Comparison of dates extrapolated by simple linear regression through Authenticated Time Signals in Widnes Warth Cores**

* see Table 1 for a list of the Time Signals used.

Table 1 Specific Time Signals in Mersey Sediment Cores*

Peak ^{137}Cs abundance	1975
Change in ratio of $^{238}Pu:^{239,240}$ Pu as Sellafield Discharges altered	1970
Take off dates for ^{241}Am and Pu isotopes as Sellafield Discharges started	1952
Appearance of significant amounts of DDT	1944

* these are in addition to the surface layer which was fixed at the time of collection. This was assumed to correspond to 1990 because of the loss of small amounts of sediment with the vegetation removed from the surface.

6.4 The Dating of Widnes Warth Cores

6.4.1 Time Signals derived from Radionuclides, Widnes Cores

The position of various radionuclides in the cores provides information from which dating schemes can be based. However, as mentioned for the stable metals, small discrepancies in detail of the profiles in radionuclide concentrations were noted by Murdock (1995). Some of these small discrepancies for the Widnes Warth cores can be clearly seen in Caesium Plutonium and Americium in Figure 6-5 and Figure 6-6.

If the concentrations of the isotopes are interpreted as being related to fixed points of times, the position of specific Time Signals can be determined in each core:

The location of the Time Signal, for 1952, which is indicated by take-off of measurable amounts of the Actinides, can be seen in Figure 6-7 & Figure 6-8.

Similarly, the changes in the ratios of Plutonium isotopes are very unambiguous (see Figure 6-9 & Figure 6-10) and provide clear Time Signals for 1970. The alterations of Plutonium isotope ratios in discharges from Sellafield are plotted in Figure 6-11 against the dates derived for Core W1 from linear regression through the Time Signals and can be seen to be a very good fit, albeit with a slight lag phase. It should be noted that the contemporary ratios present in the core seem to show the effect of reworking of the older sediments which changes the ratio in surface sediments slightly compared to contemporary inputs of the isotopes from Sellafield.

The Caesium (^{137}Cs) peaks are relatively broad but the maximum concentrations can be clearly related to Sellafield outputs and thus provide clear dating points for 1975 (Figure 6-12 and Figure 6-13).

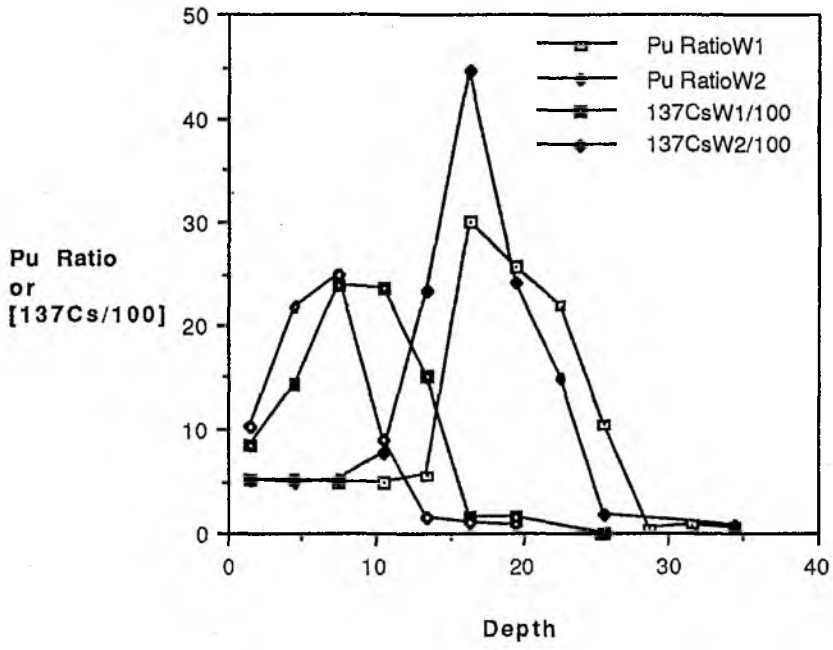

Figure 6-5 Comparison of Radionuclide (Pu & Cs) Profiles, Widnes

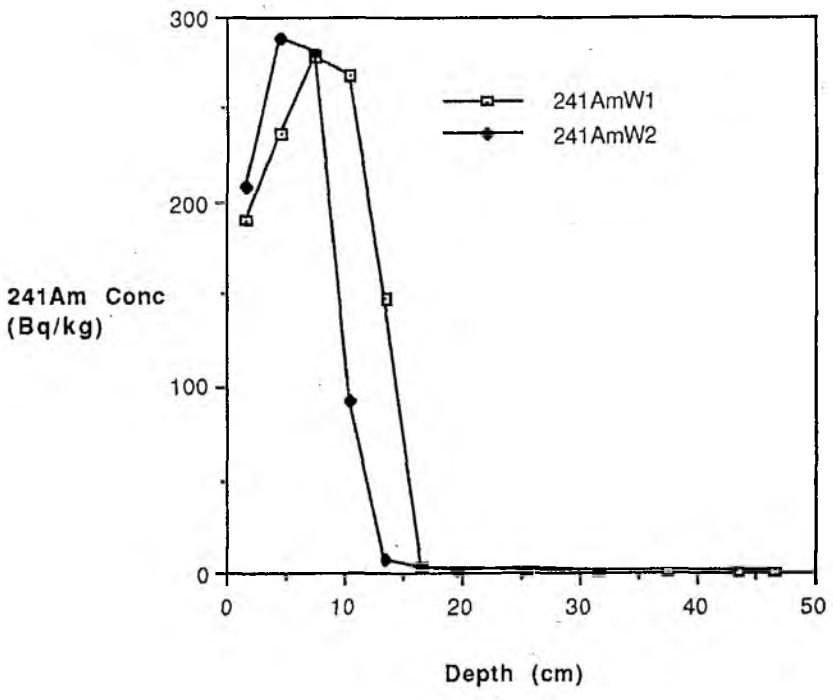

Figure 6-6 Comparison of Americium Profiles, Widnes

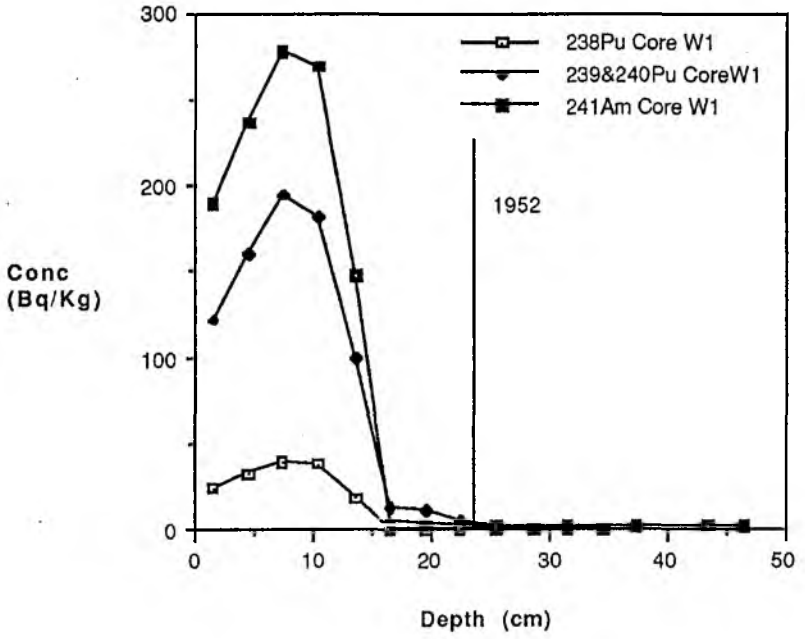

Figure 6-7 Actinide Profiles, Widnes, Core W1 showing Time Signal for 1952

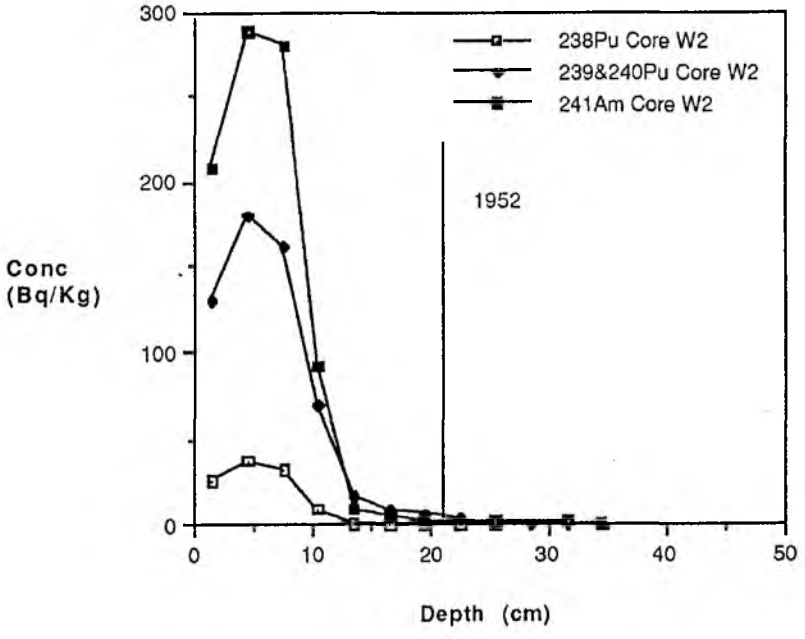

Figure 6-8 Actinide Profiles, Widnes, Core W2 showing Time Signal for 1952

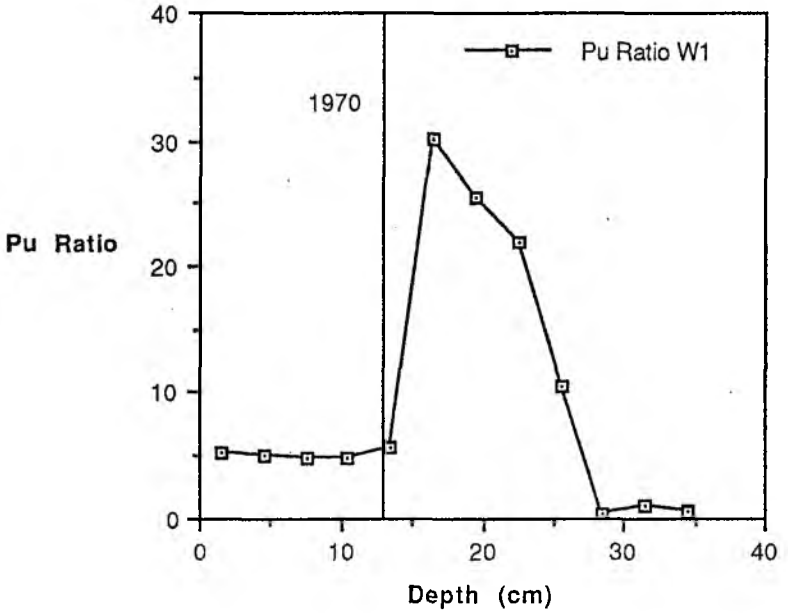

Figure 6-9 Plutonium Isotope Ratios, Widnes Core W1 showing Time Signal for 1970

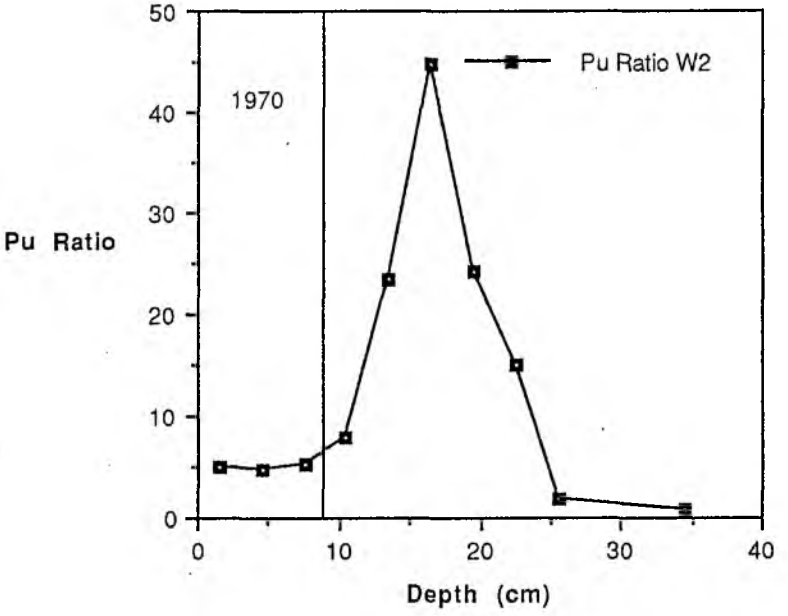

Figure 6-10 Plutonium Isotope Ratios, Widnes Core W2 showing Time Signal for 1970

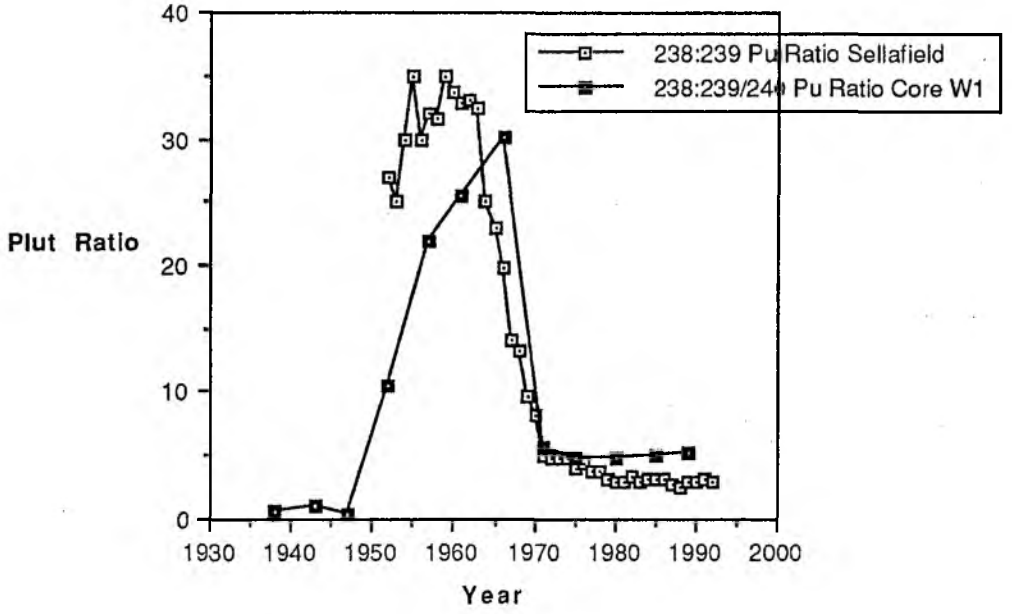

Figure 6-11 Comparison of Plutonium Ratios, Sellafield Discharge: Core W1

Notes: Dates in the core are based on linear regression through authenticated Time Signals. Sellafield Discharge ratios based on BNFL published figures. ^{239}Pu & ^{240}Pu have been measured together in the cores, whereas Sellafield figures refer only to ^{239}Pu.

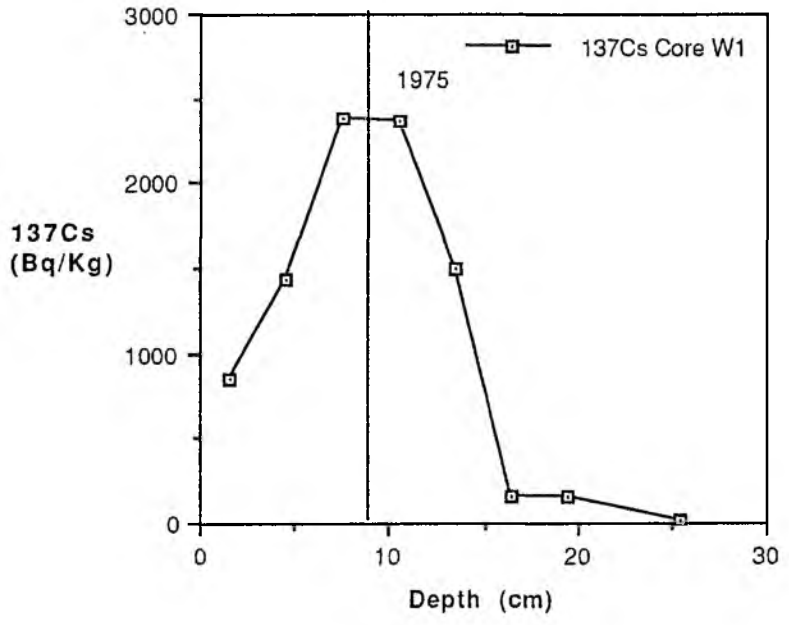

Figure 6-12 Depth Profile of ^{137}Cs, Widnes, Core W1 showing Time Signal for 1975

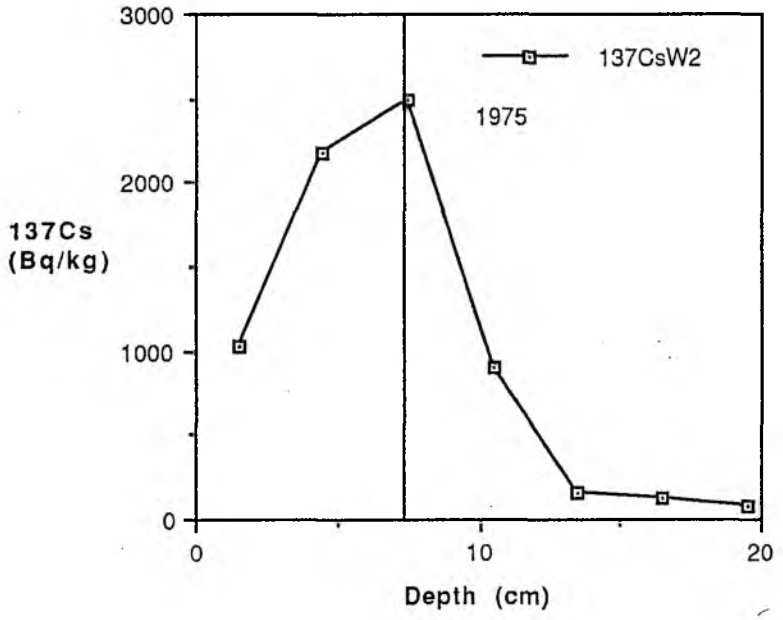

Figure 6-13 **Depth Profile of ^{137}Cs Widnes, Core W2 showing Time Signal for 1975**

6.4.2 Time Signals derived from Organochlorine Profiles in Widnes Warth Cores

There are exceptionally clear Time Signals in the DDT record in the sediments from both the Mersey (see Figure 6-14 & Figure 6-15) as well as in the Ribble. The reasons behind the massive increase in ΣDDT values are discussed in detail in Section 9. but for the purposes of developing the overall chronology, the rapid increase in concentration is suggested as a Time Signal which could be used as an extra fixed point in time because it is supported by good documentary evidence for the Mersey and a general history of use elsewhere. It is suggested that the rapid rise in concentration corresponds to a date of 1945. The assumption has been made that although there might have been small amounts of DDT entering the system before autumn 1943 from experimental manufacture or import of test quantities, the very high level of contamination must have depended on the full scale manufacture which started in November, 1943. The 'Time Signal has arbitrarily been chosen as 1945 because it is assumed that some time would have to elapse before sufficient transport would have occurred from Manchester, to contaminate the whole system. The profiles in the two Widnes Warth cores are very similar with only a small discrepancy in the depth of the peak concentration and the rapid increase in the baseline.

There are no comparable, clear documentary reasons to use the concentration profiles of the other organochlorines as Time Signals, so they are discussed in relation to their observed profiles in the appropriate sections below.

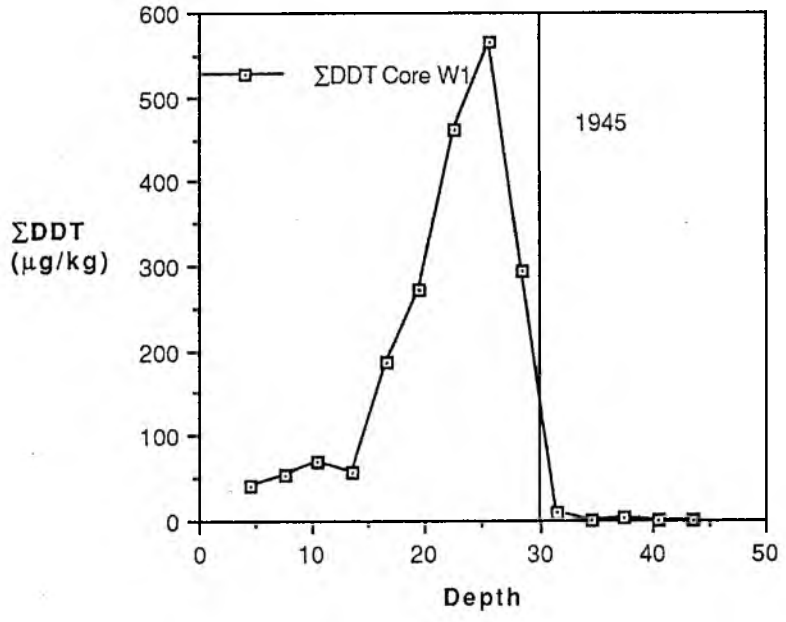

Figure 6-14 Depth Profile of ΣDDT Widnes, Core W1 showing Time Signal for 1945

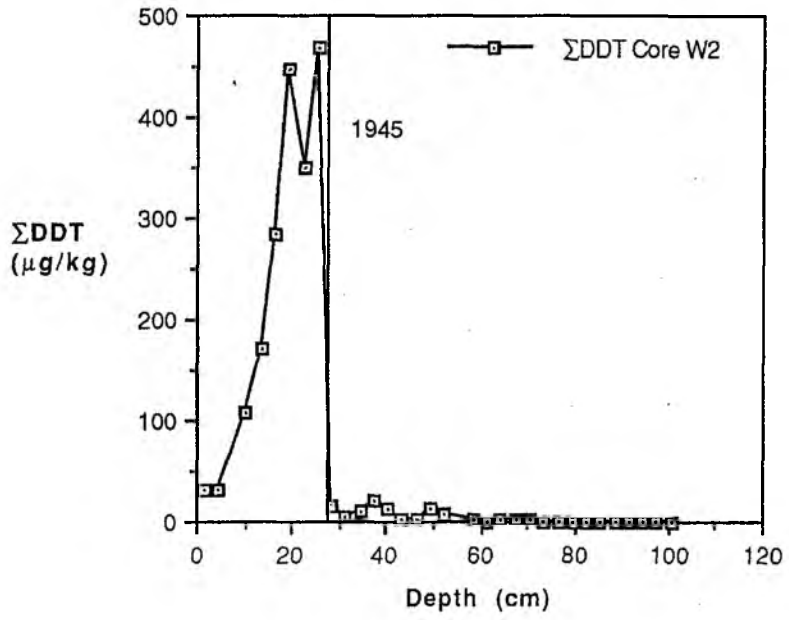

Figure 6-15 Depth Profile of ΣDDT Widnes, Core W2 showing Time Signal for 1945

6.4.3 The use of empirical pattern matching in Widnes Warth Cores

The original investigation of Murdock (1995) was designed to compare a sedimentation model derived from a series of fixed points with the profiles of various radionuclides in a series of cores. The evidence which was collected was clearest for the cores from Widnes Warth. The evidence available in 1995 was consistent with a simple linear model of deposition although a number of discrepancies were noted between cores and there were difficulties in matching the patterns in cores from different locations. A method of using polynomial regression was chosen by Murdock because it could be fitted to the available data from Widnes and also be fitted to data from elsewhere. It was assumed that simple linear deposition was just a special case.

Once the organochlorine data became available, it was obvious that there were some discrepancies and it would be necessary to re-examine the original schemes and the logic on which they were based.

To develop the interpretation of the sedimentary record further, it was noted that there were a large number of similarities in the profiles of various of the heavy metals, particularly for the Widnes cores. However, the precise spacing of the patterns were not completely consistent in pairs of cores collected very close to each other. It is evident from contemporary data that pollutant concentrations in salt marsh moods collected only a few meters apart are very similar if not identical. This suggests that concentrations stored in the sediments historically should have been similarly very close and therefore might be used to help match up chronologically similar levels in the cores. There are no *a priori* reasons to select a particular mathematical model for sediment deposition under estuarine conditions so that the fitting has been completed empirically, matching patterns by eye (see the next section).

6.4.4 Similarities in contaminant profiles between replicate cores

If the profiles of heavy metal concentrations are compared in cores taken only a small distance away from each other, it can be seen that there is a similar overall pattern of increase and decrease in concentrations of pollutants, but the patterns are not completely coincident in terms of equivalent depths (see Figure 6-16 for Arsenic) or when these depths are converted to dates (see Figure 6-17) using regressions through the Time Signals explained above (such dates are referred to as 'Calculated Dates'). Various of these inconsistencies between the two cores and between modelled dispersion of radionuclides and the observed distributions in Core W2 were already noted in the earlier study of metals in Mersey sediments (Murdock, 1995) but the reasons for them could not be resolved.

The original scheme developed by Murdock, included a number of dates fixed by slices containing 'features' to which known dates could be applied. At the top of the core, these principally relied upon known facts about the radioisotope emissions from Sellafield. However, in the middle and bottom region of the cores, the suggested dates were based on items for which dates could only be rather imprecise such as changes in the emissions of metals because of general industrial changes for which there is no precise date. The small number of fixed points towards the top of the cores was not much help in fixing dates towards the bottom of the cores (and still remains a problem now).

Information on the distribution of organochlorine contaminants was not available to Murdock (1995) but it confirms the general principles involved which are apparent for the metals. The organochlorine contaminants have very similar concentration profiles in the Widnes Warth pair of cores, and there are only small differences in the position of peak concentrations down the core. Although, the discrepancies in depth profiles for the organochlorines are smaller than those for the heavy metals (see Figure 6-18 for DDT) they do not go as far back in time.

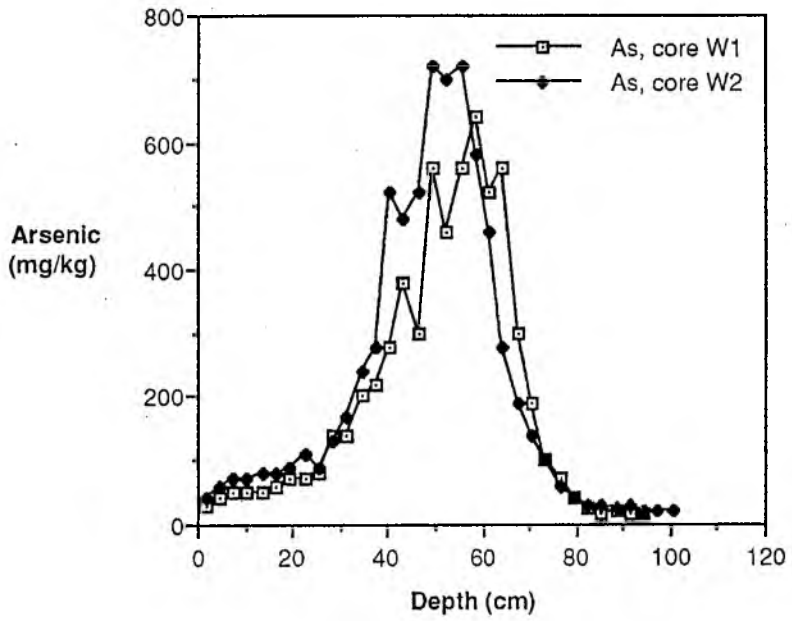

Figure 6-16 Arsenic Concentration Depth Profile, Widnes

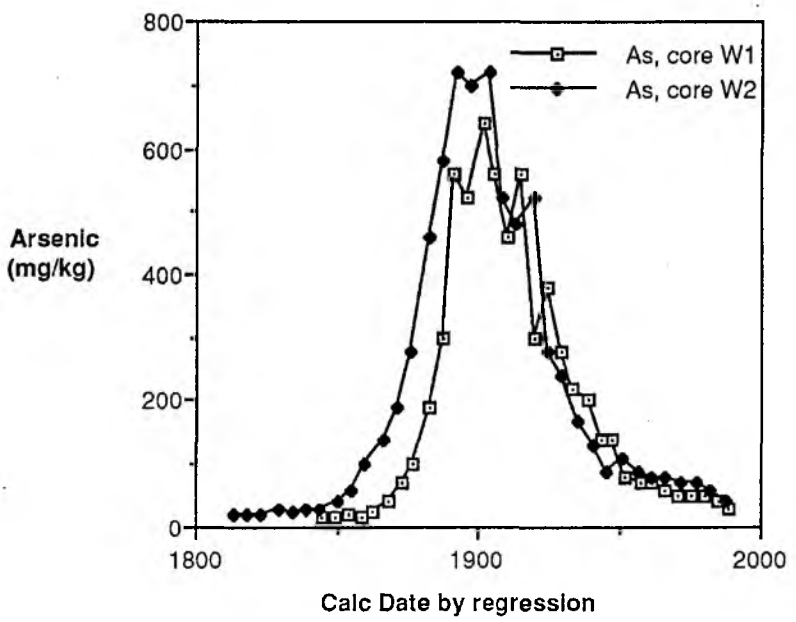

Figure 6-17 Arsenic Concentration Profiles, Widnes, based on dates calculated from regressions through 'Time Signals'

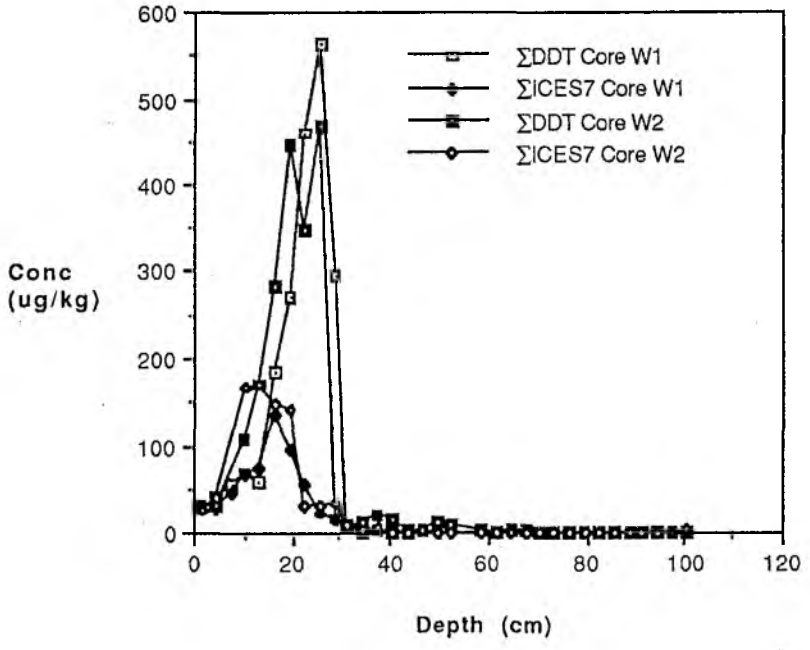

Figure 6-18 DDT & PCB Concentration Depth Profiles, Widnes

The Lead profile was used as a starting point to match the contaminant concentrations of the two cores to each other in an empirical manner (Figure 6-19). From first principles, lead would be expected to be very immobile in the sediment cores and of the data available, the profile for lead contains the most 'features' in the pattern of

contamination. Core 1, which Murdock and subsequent work had shown to fit a linear deposition model very well, was used as the master dating scheme, and Core 2 dates were adjusted arbitrarily until the lead concentration pattern of the two cores fitted in terms of concentration (Figure 6-20).

The data for the other metals was then plotted against the new dates and compared with the equivalent data for Core 1 (see Figure 7-2 to Figure 7-6). The results were that in each case, there was a radical improvement in the coincidence between 'features' such as peaks and troughs in concentrations. Such a finding implies that the record of pollutant concentration in cores collected in close proximity must be very similar but there may be small discrepancies in the concentration with depth profiles due to variation in the rate of sedimentation over distances of only a few metres. Such a finding should not really be surprising, considering the way in which saltmarsh vegetation grows and the small scale physical features which develop on the marsh and subsequently disappear.

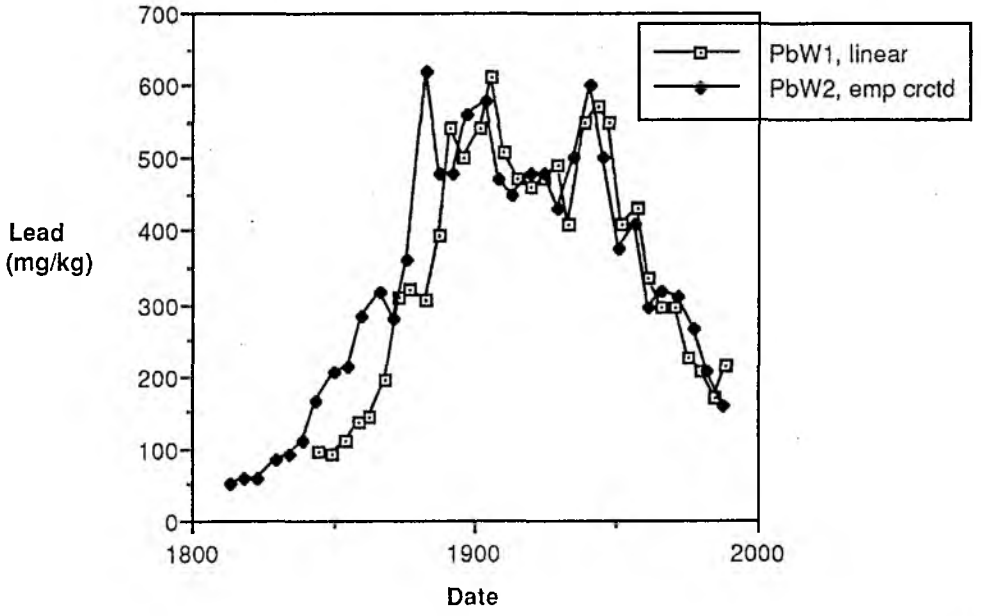

Figure 6-19 Lead Profiles, Widnes, based on regressions through authenticated Time Signals

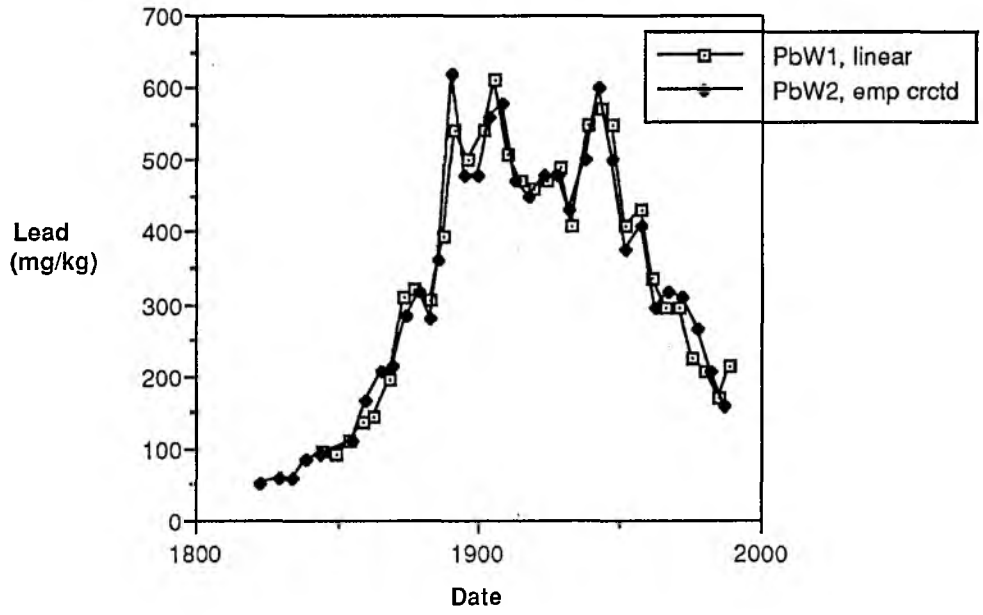

Figure 6-20 Comparison of Lead profiles, Widnes, after applying Empirical corrections to Core 2

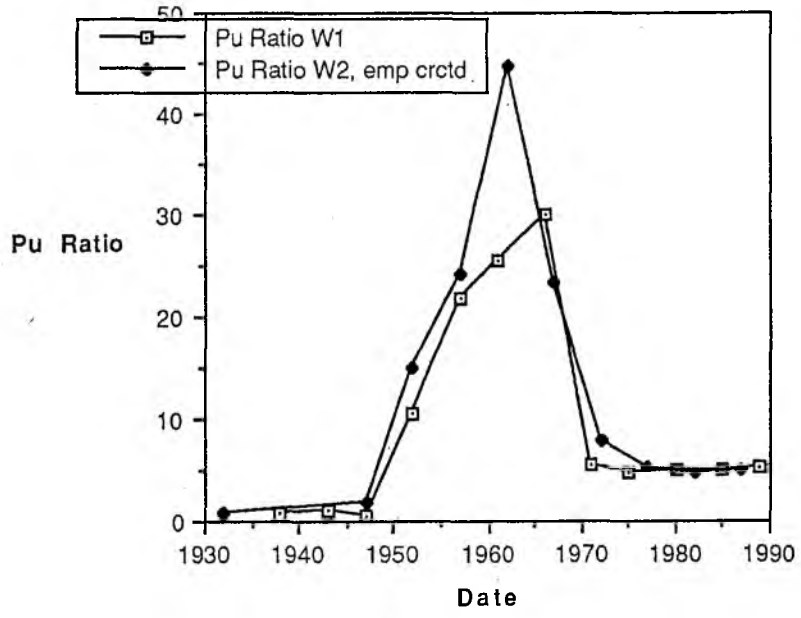

Figure 6-21 Plutonium isotope ratios in two cores from Widnes with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1

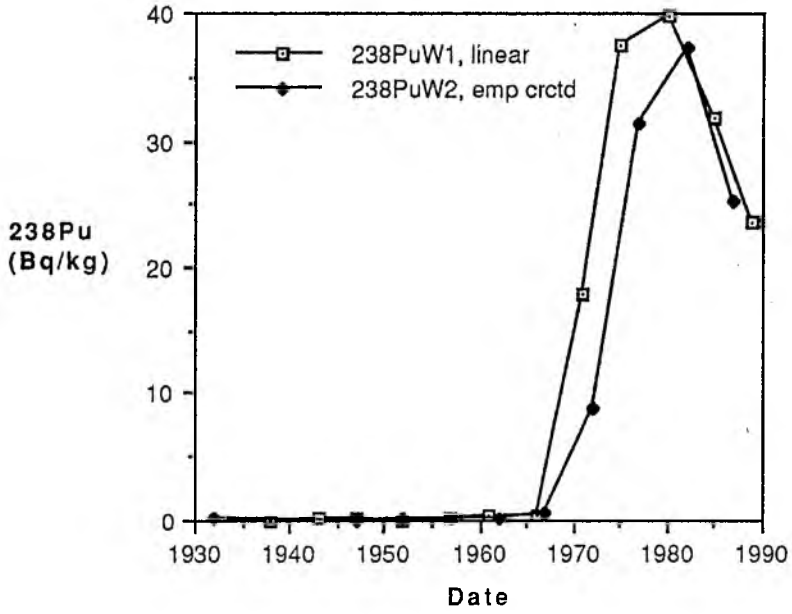

Figure 6-22 **^{238}Plutonium profiles in two cores from Widnes with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

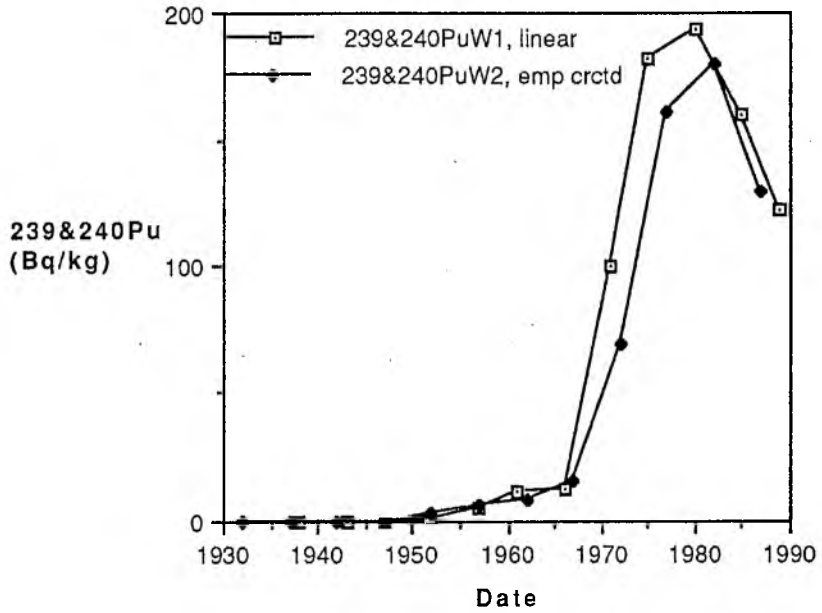

Figure 6-23 **^{238} & ^{240} Plutonium profiles in two cores from Widnes with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

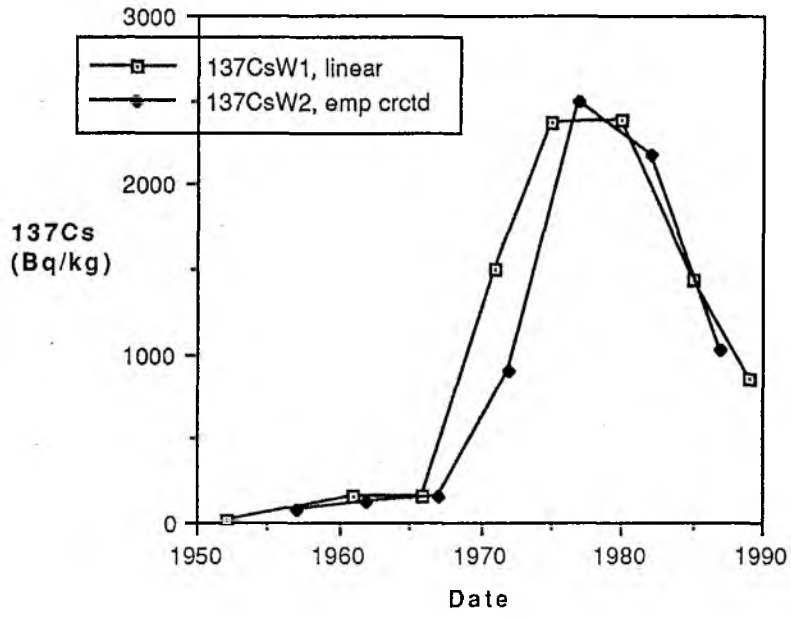

Figure 6-24 **^{137}Caesium profiles in two cores from Widnes with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

6.4.5 Choosing a Chronology for Widnes Warth cores

The adjustments resulting from matching pollutant patterns discussed above result in closer fits between pollutant date profiles in what are effectively replicate cores but by itself this does not establish an absolute dating scheme. The continued relatively close similarity between the two Widnes Warth cores and the overall approximation to linear deposition rates leads to the suggestion that at the current level of understanding, with the data available, the best available hypothesis is that a linear rate of sediment deposition has occurred through the period of history covered by the cores. Their fortuitous similarity may hide the fact that there have been significant changes in deposition rates during the period but the obvious differences with the changing deposition rates both at Ince and Banks Marsh give some confidence that the hypothesis of linear deposition at Widnes is likely to prove correct. However, this will only be revealed if further methods for dating the lower levels of sediment cores can be achieved.

6.4.6 The implications of changing the basis for dating the sediment cores

Murdock (1995) concluded that the best way of modelling the dates in the sediment cores was by fitting a third order polynomial regression through the fixed dates which he had determined using a variety of methods (see Figure 6-25). The two fitted lines were very similar to each other despite there being small but obvious discrepancies in the depth of the points used in the equations. The comparison of the authenticated dates in the two Widnes cores (Figure 6-26) shows the apparently linear model of deposition for core W1, the small discrepancies with core W2 in the depth at which they occur and also the non-linear nature of deposition in core W2.

The apparent similarity of the two lines produced using the polynomial regression is partly the mathematical effect of attempting to fit a line through data which contains one point (that based on 'metal take-off') which is a very long way away from the others resulting in very high 'leverage' of that point. The differences in dating of the two Widnes Warth cores produced by linear regression through the Time Signals (including that based on DDT) can be seen in Figure 6-27 and also compared with the result of the empirical fitting to Core W2 referred to above. The larger differential with a simple regression fitted through the time signals available to Murdock (1995) (not including DDT) can be seen in Figure 6-28 and Figure 6-29 together with the polynomial dating which he eventually used. It can be seen that the major differences with the linear chronology proposed for use here (see Section 6.4.8) are only in the deeper half of the core. The dating in the upper half of the core is very similar with either scheme.

It is worth noting that the changes imposed on the dating of Widnes Warth core W2 by pattern shifting, would decrease some of the discrepancies noted by Murdock (1995) in the coincidence of the Actinide concentrations with those predicted by the BNFL model.

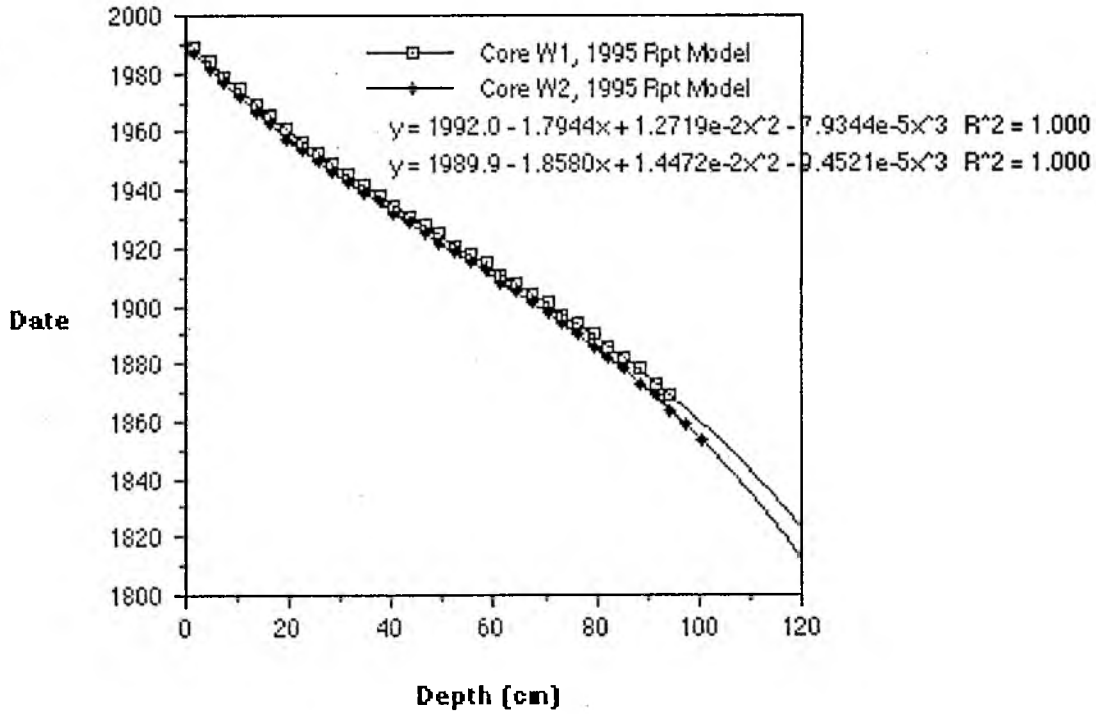

Figure 6-25 Final Dating Profiles reported by Murdock (1995), Widnes, Core W1 & W2

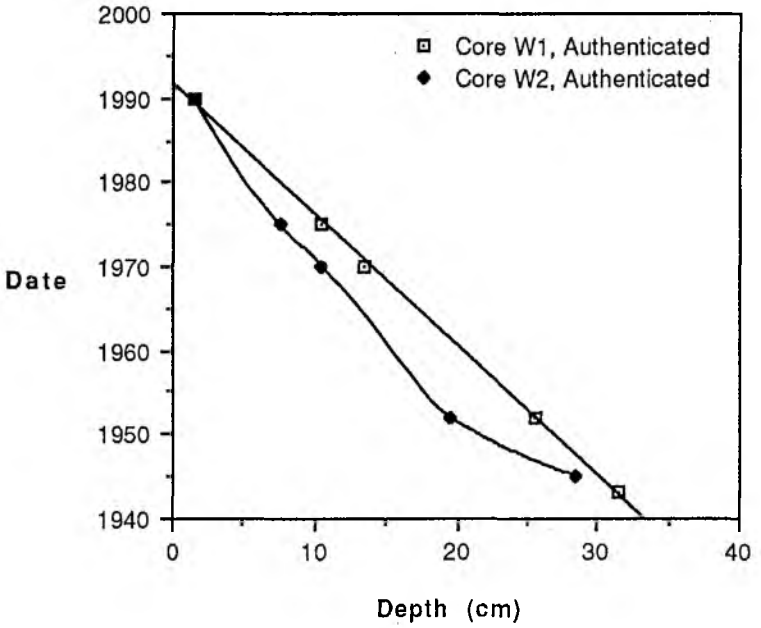

Figure 6-26 Comparison of the position of the Authenticated Time Signals in Widnes Warth, Cores W1 & W2

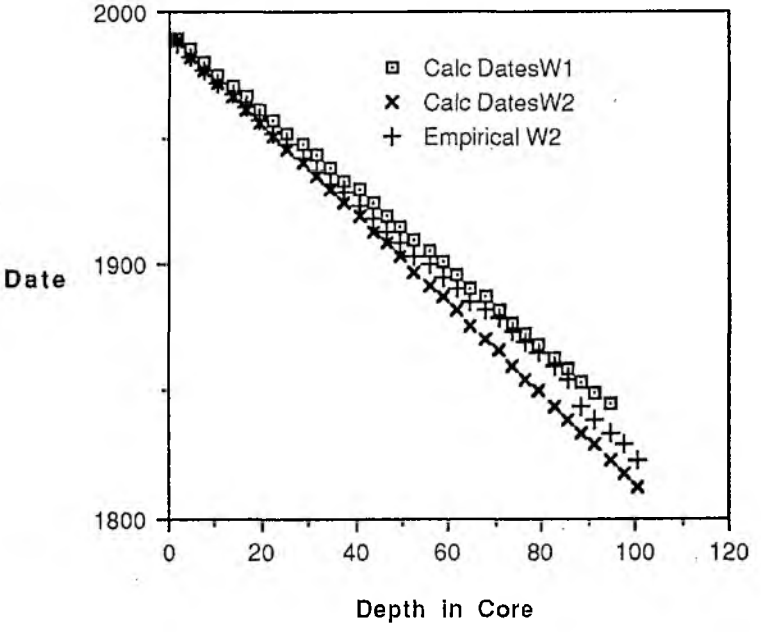

Figure 6-27 Comparison of calculated date in two cores (W1 & W2) from Widnes with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1

NOTE: calculated dates are derived from simple regression through the authenticated 'Time Signals'

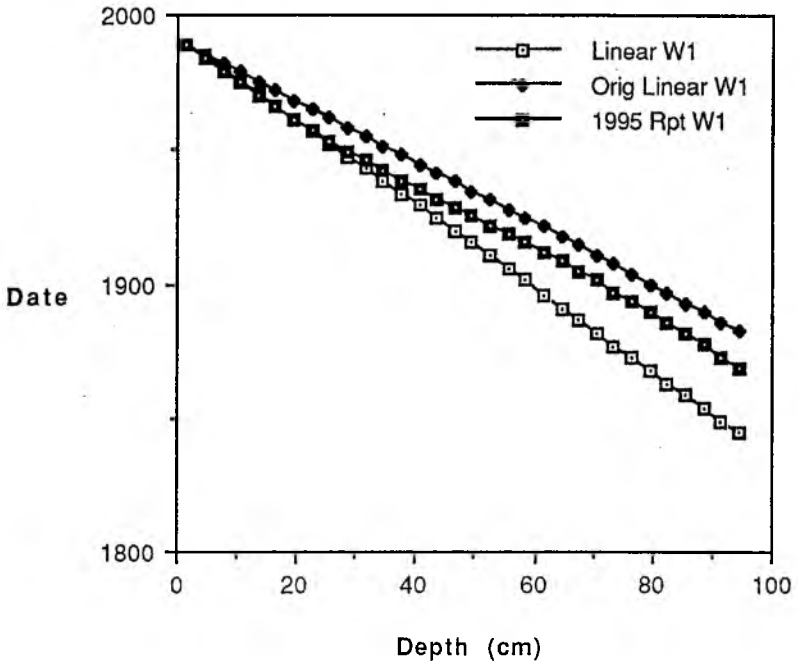

Figure 6-28 Comparison of Dating Profiles obtained by using different assumptions, Widnes, Core W1

NOTES:

Linear W1 - simple linear regression through all of the Time Signals now available for Core W1

Orig Linear - from Murdock (1995) data - linear regression through the fixed dates then available

1995 Rpt W1 - 3rd order polynomial presented in (Murdock 1995) using the fixed dates together with the metals 'take-off' point - attributed to 1840.

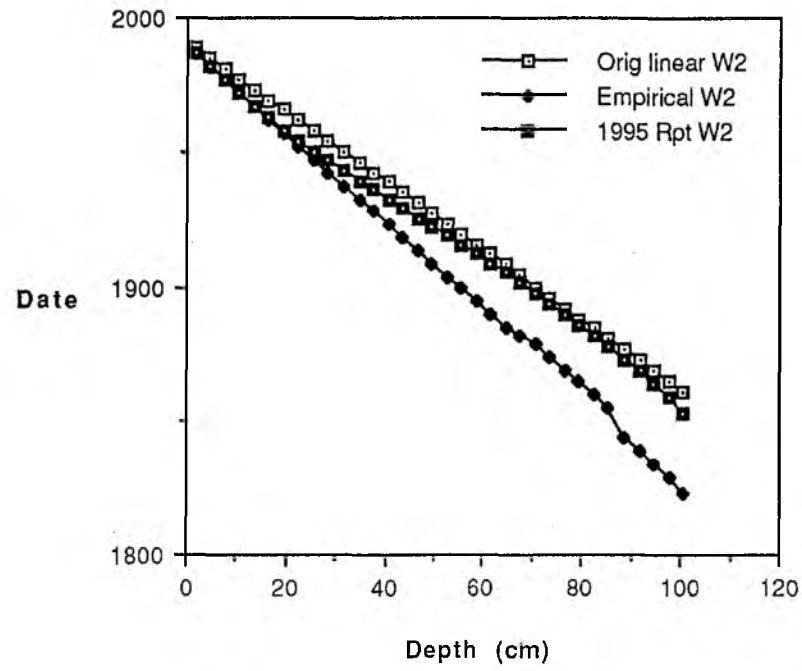

Figure 6-29 Comparison of Dating Profiles obtained by using different assumptions, Widnes, Core W2

NOTES:

Orig Linear W2 - from Murdock (1995) data - linear regression through the fixed dates then available

1995 Rpt W2 - 3rd order polynomial presented in (Murdock 1995) using the fixed dates together with the metals 'take-off' point - attributed to 1840.

Empirical W2 - derived in this report from empirical fitting of Core W2 data to Core W1 data which has been assumed to be linear

6.4.7 General Conclusions on the dating of cores

The cores contain a coherent record of past contamination in the form of sequentially laid down layers of sediment.

There is a consistent and logical pattern in the observations based on radionuclides, stable heavy metals and hydrophobic organic chemicals. This implies that once fixed in the sediment, the pollutants are relatively immobile. (However, this does not imply that all pollutants behave similarly).

From the evidence discussed above, it is concluded that although there is a similar pattern of contamination through time in these two cores from Widnes Warth, collected only a few meters apart, the chronology of deposition in the two cores differs by small amounts.

As a consequence of the small differences in deposition rate, simple averaging of contaminant concentrations from equivalent depths in the two cores is not appropriate since it would lose information.

With the availability of a new 'fixed date', that for the appearance in the environment of DDT, the linear dating schemes were recalculated using only the dates in the upper part

of the core for which there was firm data. This has the advantage of removing the point at the base of the core for which there is least precise evidence.

The regression lines through the fixed points now provide the best available estimate for a linear deposition model and a chronology based on it.

It is reassuring that there is not very much difference in the dating of the two cores, even when extrapolated back to the base of the cores.

The same pattern of events has occurred in replicate cores back to their base, but although events back to the 1940s appear to fit well to an absolute chronology, the further back in time from there, the more the chronology 'floats' in time. It is however reasonable to assume that the chronology goes back well into the 19th century and seems to cover the majority of the industrial history of the Mersey Estuary.

6.4.8 The Final dating scheme proposed for Widnes Warth Marsh

The available data suggests that there is a very close correspondence in heavy metal concentration between replicate cores taken in close proximity but there have been small differences in sedimentation rate through the length of the cores.

A simple 'floating' chronology has been constructed which fits the linear model of deposition at Widnes Warth quite closely (see Figure 6-30).

The data from replicate cores can be fitted to the floating chronology by empirical adjustment to the dates at depth in the cores.

The floating chronology can be fixed to absolute dates at only a small number of points in the upper layers.

With the data currently available, the best available absolute chronology has been obtained from the regression line fitted to the Time Signals derived from the Sellafield radionuclides. In the absence of any better data, the regression line through data for core W1 has been taken as the most appropriate base for the chronology because all of the available Time Signals for this core fit close to the regression line.

It is recognised that THE CLOSENESS OF FIT of the Time Signals in Core W1 to a straight line MAY BE PURELY FORTUITOUS.

To determine how well the chronology developed here represents reality will have to await the dating of lower levels in the cores based on alternative methodologies.

Once empirically adjusted, the cores show a very clear historical pattern of contamination by all of the heavy metals.

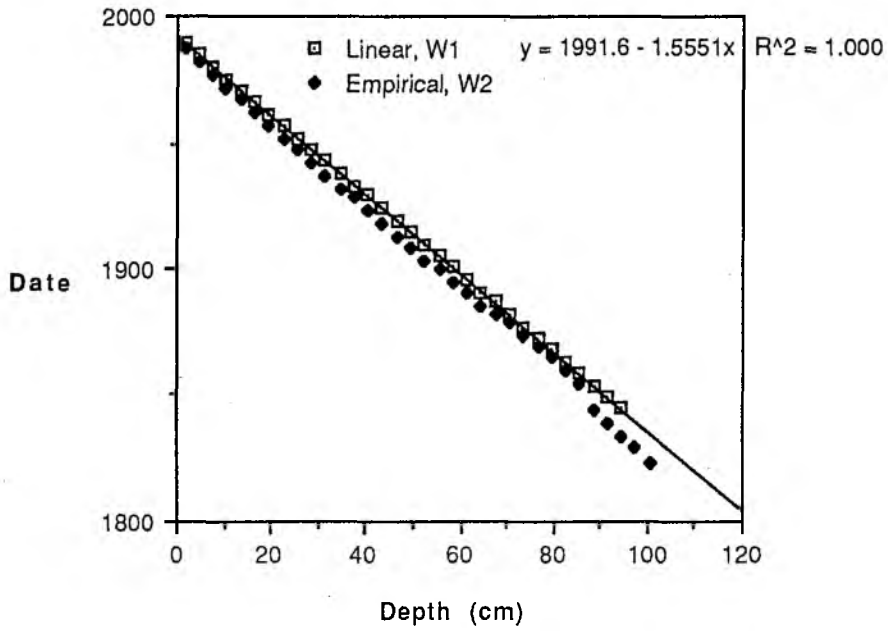

Figure 6-30 Final Dating Profiles for Cores W1 & W2 from Widnes Warth marsh

6.5 The Dating of Ince Marsh Cores

The dating of Ince Marsh cores was problematical to Murdock (Murdock, pers. comm.) because of the lack of the obvious features in the metal concentrations which he measured, making it very difficult to attribute any date accurately to the bottom of the cores. He eventually concluded that the cores went back to around 1850 at 1 meter depth. However, when organochlorine data became available in this study, (see Figure 6-31) it was immediately obvious that either such an early date was substantially wrong or organochlorines were behaving differently to metals in cores. For various reasons outlined above, this possibility was thought to be unlikely.

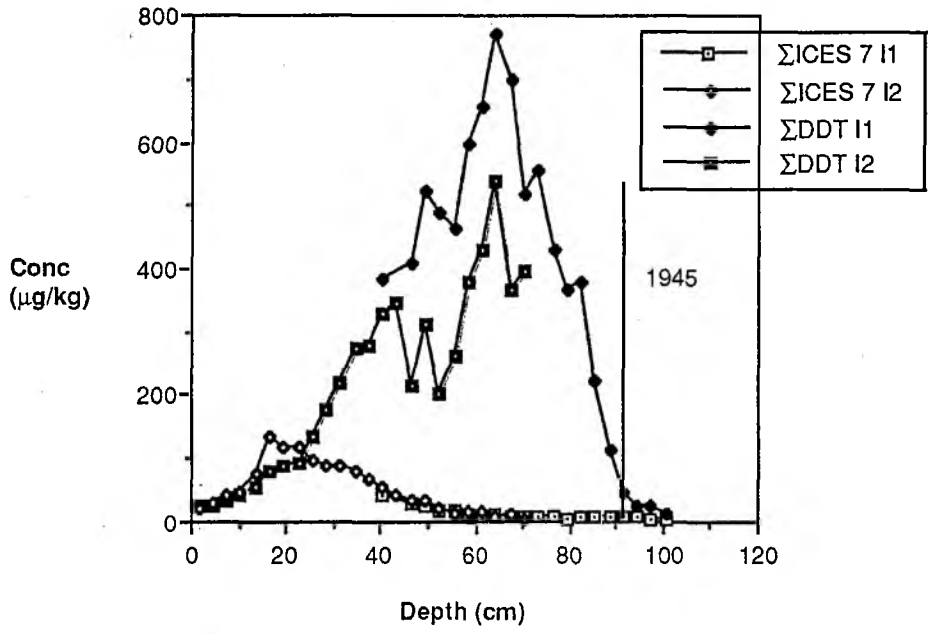

Figure 6-31 Time Signal for 1945 in Ince cores, based on appearance of ΣDDT

For reasons associated with the costs of analyses, the analysis of replicate cores from Ince Marsh could not be completed in its entirety. The first core analysed (I1) was relatively short and contained high concentrations of DDT down to the base. The second core was analysed from the base upwards until sufficient data had been obtained to provide good overlap in the middle. It can be seen that the combination of DDT data and PCB data provides a high degree of confidence that a similar profile of contaminants exists in both cores, despite some discrepancy in absolute concentrations of the DDT group compounds. This discrepancy in concentration might be real but could also have a component due to the difficulty of quantifying the DDT concentrations in what were very dirty samples containing hundreds of organochlorines in a difficult matrix. In this respect, Ince Marsh Cores were slightly more problematical than cores from Widnes Warth. At this stage, it is not possible to quantify the component which might be due to differences as a result of particle size and composition differentials between the two cores.

Despite the difficulties outlined, it was possible to determine the location of the other Time Signals in the cores (see Figure 6-31 to Figure 6-34) so that the conclusion is reached that Cores I1 and I2 have accumulated sediment at very similar rates through the period of study.

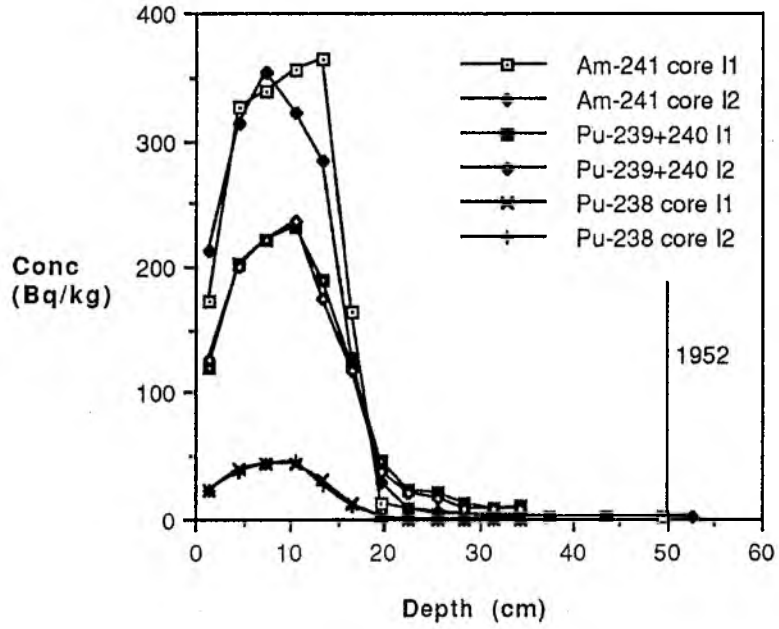

Figure 6-32 Time Signal for 1952 in Ince cores, based on appearance of Actinides.

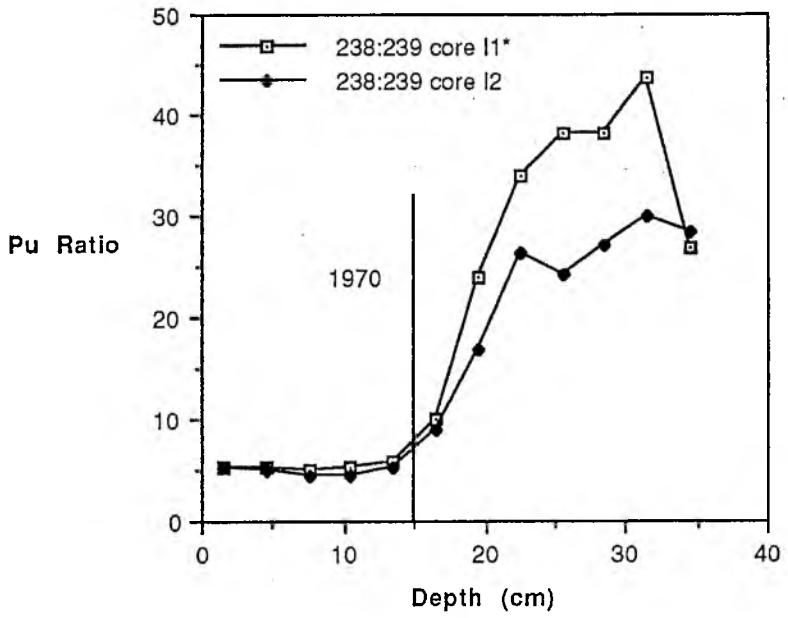

Figure 6-33 Time Signal for 1970 in Ince cores, based on Plutonium isotope Ratio

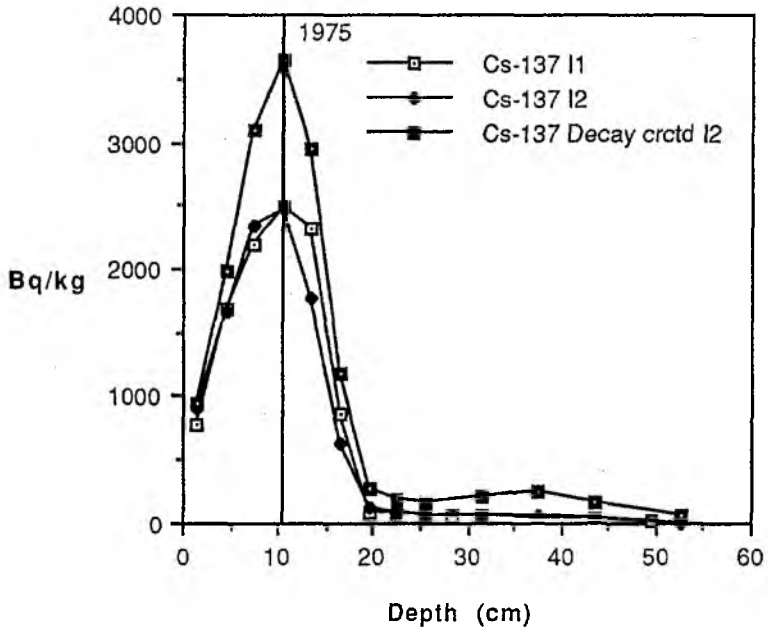

Figure 6-34 Time Signal for 1975 in Ince cores, based on ^{137}Cs
(showing the effect of correcting for the decay of the isotope over time)

6.5.1 The Final Dating Scheme proposed for Ince Marsh Cores

The depth position of the time signals in the replicate Ince cores proved to be very similar to each other where data for the two cores were available. However, it proved not to be very easy to fit a mathematical line through the time signals. It was very clear that the sedimentation rate could not have been linear but neither was it a close fit to any simple mathematical model, so it was decided that with one time signal (that for DDT) available near to the base of the cores, interpolation of the remaining dates was arguably the best method of developing a dating scheme. This can be seen in Figure 6-35. This scheme implies that the base of Core I2 (the longer of the two) only goes back in time to approximately 1943. Sedimentation rates in the 1940s must have been very high, starting to decrease in the 1950s, with the decrease in rate continuing to the surface.

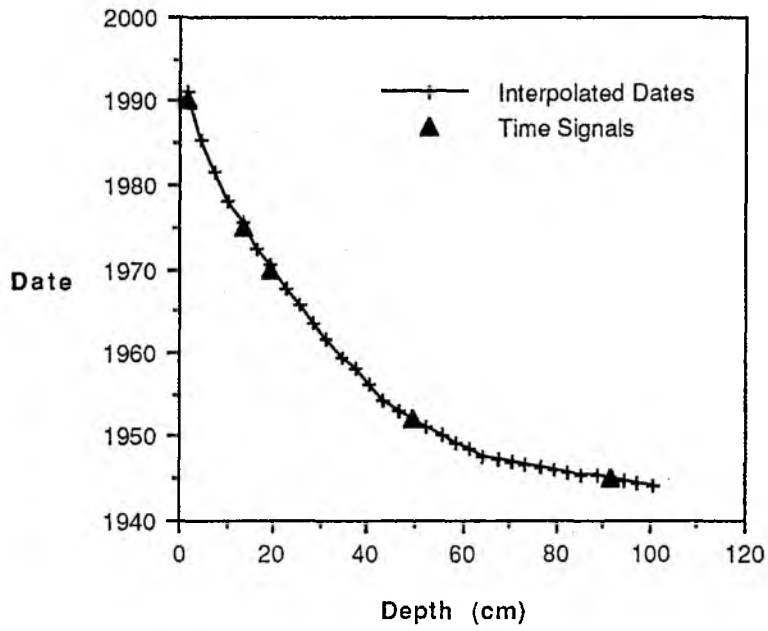

Figure 6-35 Final Dating Scheme for Ince Marsh Cores using interpolated dates

6.6 The Dating of Banks Marsh Sediment Cores

Using the idea that it was possible to suggest a 'take-off' date for metal contamination arising from industrial use, Murdock (1995) eventually concluded that the Banks Marsh cores went back to around 1850 at 1 meter depth. However, when the data for organochlorines (particularly that for ΣDDT) became available in this study, (see Figure 6-31) it was immediately obvious that either the original assumptions were wrong or organochlorines were behaving differently to heavy metals in sediments. For various reasons outlined above, this latter option was unlikely.

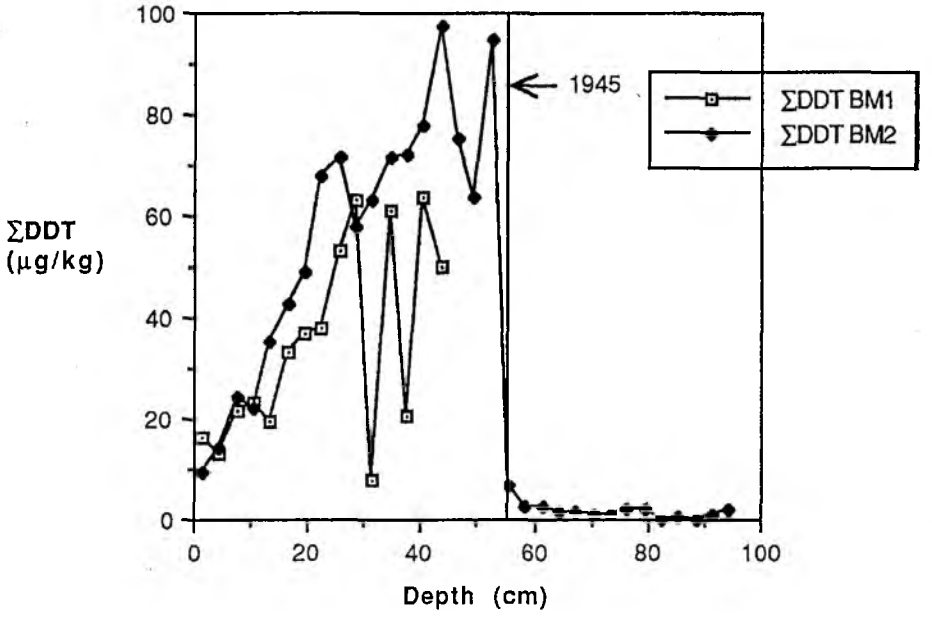

Figure 6-36 Time Signal for 1945 in Banks Marsh cores, based on appearance of ΣDDT

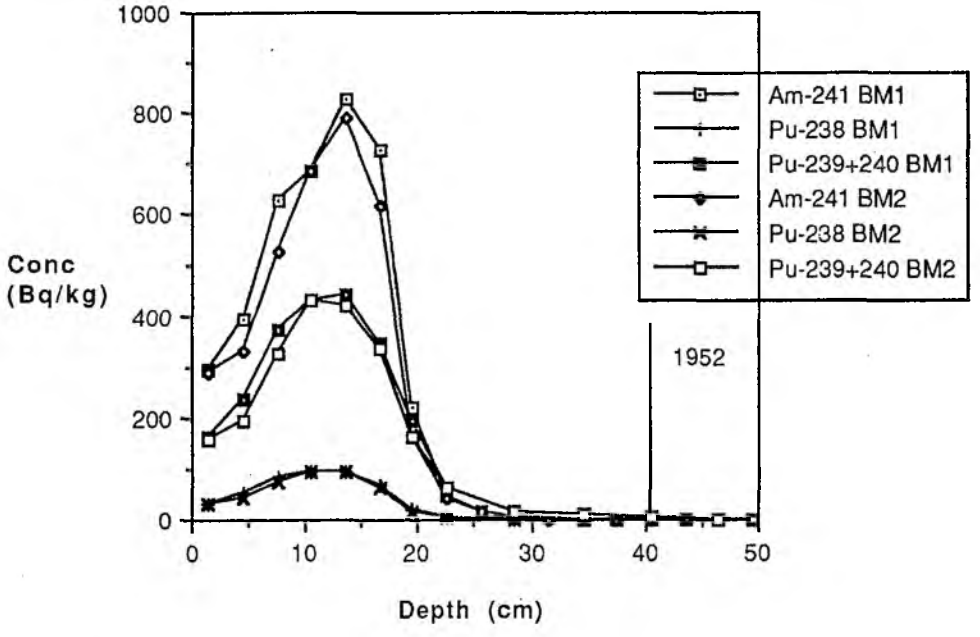

Figure 6-37 Time Signal for 1952 in Banks Marsh cores, based on the appearance of Actinides

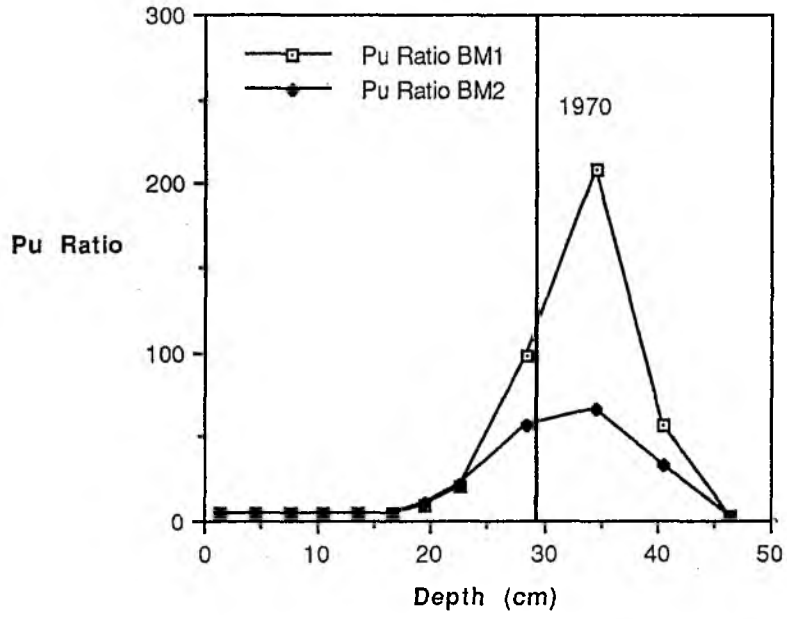

Figure 6-38 Time Signal for 1970 in Banks Marsh cores, based on Plutonium isotope Ratio

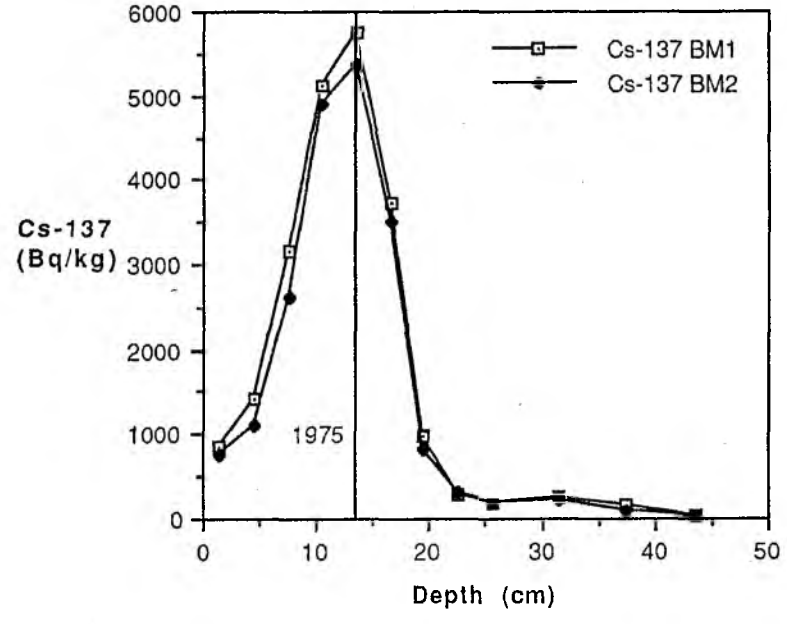

Figure 6-39 Time Signal for 1975 in Banks Marsh cores, based on ^{137}Cs

6.6.1 Final Dating Scheme proposed for Banks Marsh Sediment Cores

The depth position of the time signals in the replicate Banks Marsh cores proved to be very similar where the data for both cores were available. However, as was the case for Ince Marsh, it proved not to be very easy to fit a mathematical line through the time

signals. It was very clear that the sedimentation rate could not have been linear but neither was it a close fit to any simple mathematical model, so it was decided that interpolation of the dates through the time signals was arguably the best method of developing a dating scheme although it was necessary to extrapolate from the last time signal (1945) to the base of the core. The results can be seen in Figure 6-40. The justification for assuming a linear rate of deposition from 1920 to 1945 is relatively weak apart from the fact that it does fit with the last two of the time signals. There is also a known problem, in that the last few slices at the bottom of the cores from Banks Marsh were described by Murdock as very sandy, a fact which is borne out by the very low organic matter suggested by the LOI data (see Section 6.2). Since most of the pollutants studied will become preferentially associated with fine organic rich particles, the early rapid increase in pollutant concentrations in the cores discussed below is probably the result of this effect.

This scheme implies that the base of the cores can only go back in time to approximately 1920, possibly not even this early if the sandy layers were deposited at a faster rate than the subsequent muds. In general, the early sedimentation rates were higher than those applying since 1960 when there appears to have been a significant decrease in the rate.

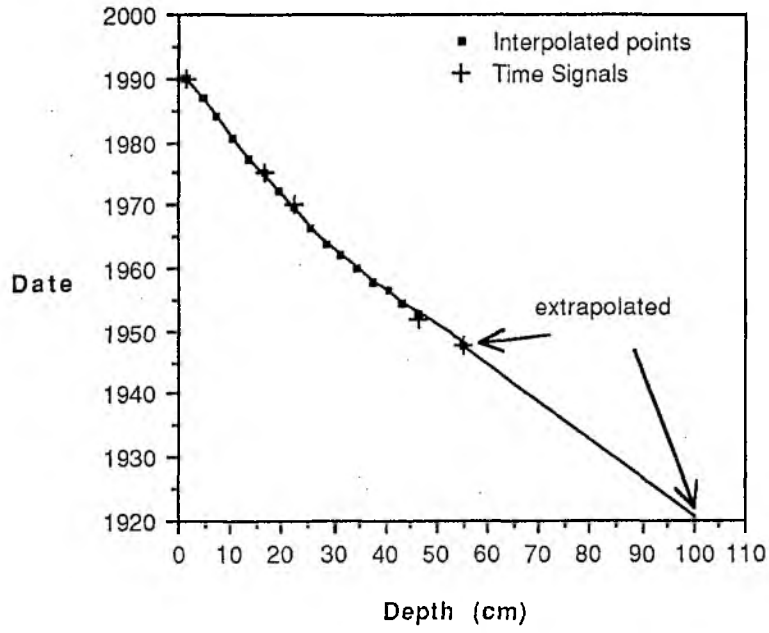

Figure 6-40 Final Dating Scheme for Banks Marsh Cores using both interpolated and extrapolated dates

Adoption of the suggested dating scheme would have major implications for the dates reported in Murdock (1995). These can be seen very clearly in Figure 6-41. The net result is a major alteration in the perception of the contamination of the Ribble in comparison with that of the Mersey. This is considered in detail in Section 11.

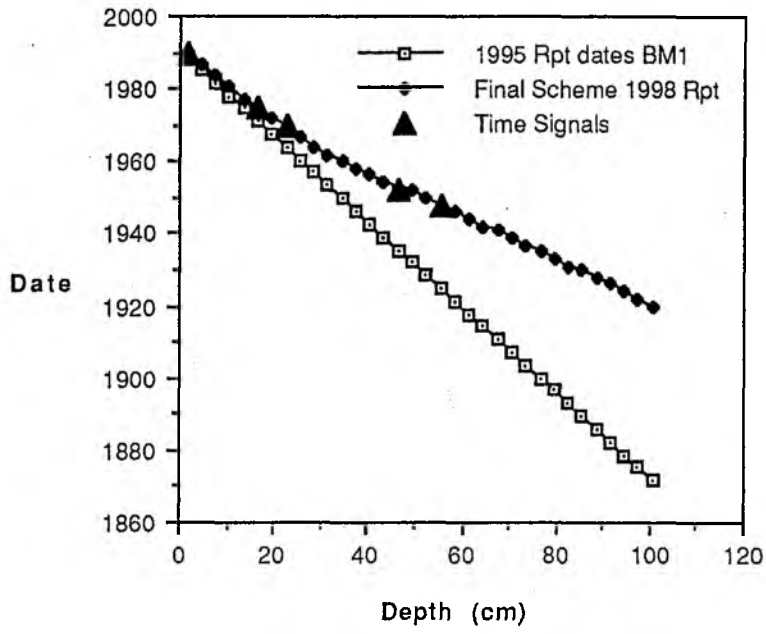

Figure 6-41 Comparison of Dating Profiles for Banks Marsh obtained by using different assumptions

6.7 General Discussion of Dating Sediment Cores

Buerskens et.al., (1993) examined the geochronology of priority pollutants in a sedimentation area of the Rhine river. The cores were dated by radioactive Cs profiles but these could be cross checked by specific physical characters formed by the draining of the original marsh system and the creation of a freshwater lake.

The results presented in previous sections lead to the conclusion that deposition of sediments has not been the same at all of the locations studied. This is unsurprising since major differences in the contamination record within cores has been a constant feature of investigations of this type (eg Cundy et.al., 1997). In many studies, this has been connected with the very different sedimentary conditions pertaining at the collection points. However, this study involves only cores collected from carefully chosen sites which were known to have been stable for long periods of time. They were all sites where the sediments which have collected have all been fine-grained, organic-rich muds. Thus they are all likely to be very comparable without the problems of normalisation which are involved if the sediments being compared include radically different grain sizes.

Another feature of this study which lends extra confidence to the interpretation is the use of replicate cores taken from points only a few metres apart. From the results presented for all the types of pollutants studied, it can be seen that the sedimentary processes are faithfully reflected with a surprising degree of consistency within a single location.

Taking this into account, it then seems acceptable to accept radically different models of sedimentation as occurring at the different locations studied, despite the need to argue that sedimentation has occurred in both a linear and curvilinear manner at different sites within the same estuary. This has quite clearly arisen because of the different physical histories of the locations. Other workers have found non-linear sedimentary histories

elsewhere. For example, Axelman et al (1995) conducted a time trend analysis of PAH & PCB sediment fluxes in the Northern Baltic Proper using a number of different dating methods including radionuclides and counting laminae within the sediment layers. They showed curvilinear results for Cs, Pu and ^{210}Pb (although it should be noted that their sedimentation rates were very low in comparison to those in the estuaries being studied here.

The sedimentation rates reported here are well within the range reported around the world, including sites where the rate has been measured directly (eg Cahoon et.al., 1996).

7. The revealed history of contamination by heavy metals in the Mersey Estuary

7.1 The detailed history of individual metals

Full details of the industrial history of the metals are given in Murdock, 1995.

7.1.1 The history of Lead contamination of the Mersey Estuary

Lead concentrations (see Figure 7-1) were increasing from early in the 19th century, accelerating from 1850 with the first major peak in concentration being reached before the end of the century. There was a second peak of similar concentration preceding World War I with a major decline in the inter war years, The peak in concentration produced during World War II was almost as high as the earlier two but was followed by a rapid decline which continued more or less through to the surface of the core at around 1990. Contemporary concentrations remain well elevated above the original baseline.

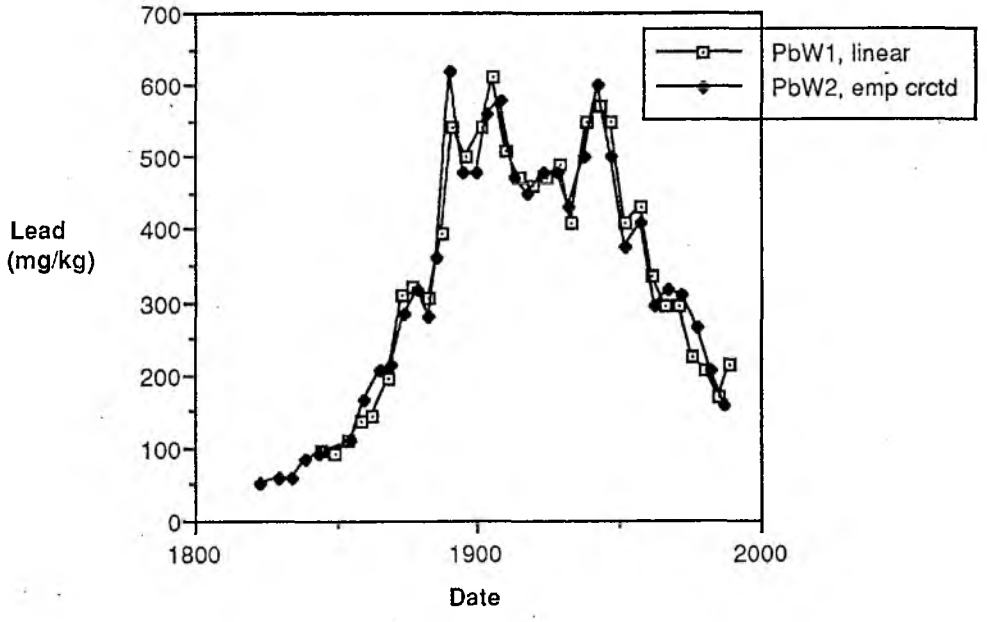

Figure 7-1 **Lead in replicate cores, Widnes, after applying Empirical corrections to Core 2 to match the patterns of contamination**

7.1.2 The history of Arsenic contamination of the Mersey Estuary

Arsenic concentrations (see Figure 7-2) only started to increase in the 1870s, accelerating rapidly to reach peak concentrations by the end of the century. These stayed high for a few years before declining rapidly after World War I. There is no evidence of a second peak for this element during World War II so that the decline continued rapidly to the 1950s with a much slower decline to the surface of the core at around 1990. Contemporary concentrations now approach those of the original baseline before industrialisation.

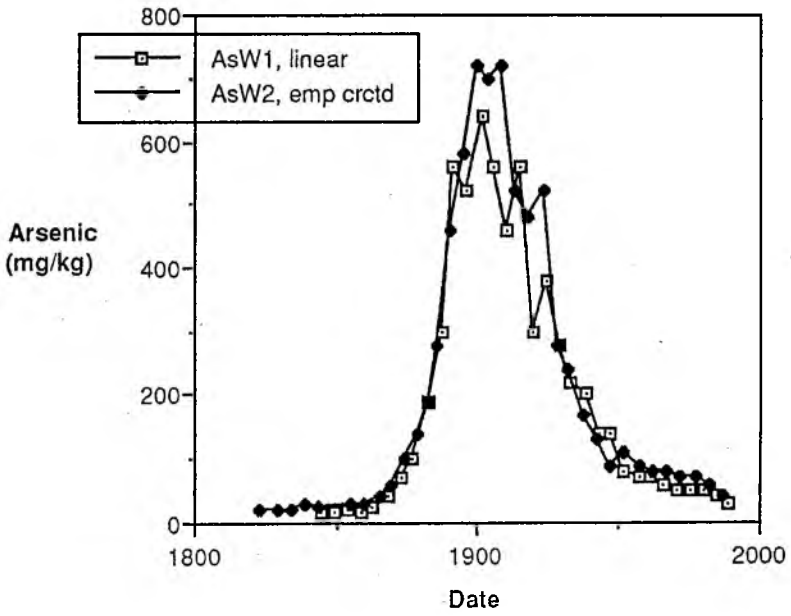

Figure 7-2 **Arsenic in replicate cores, Widnes, with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

7.1.3 The history of Chromium contamination of the Mersey Estuary

Chromium concentrations (see Figure 7-3) started to increase only in the second half of the 19th century after 1850. An initial steep increase to a subsidiary peak around 1875 was followed by some decline before a very rapid increase in the early years of the 20th century. A period of rapid decline followed by continuous but less rapid decline was interrupted by slight increases in the years before World War II. Concentrations around 1990 were still much higher than before industrialisation.

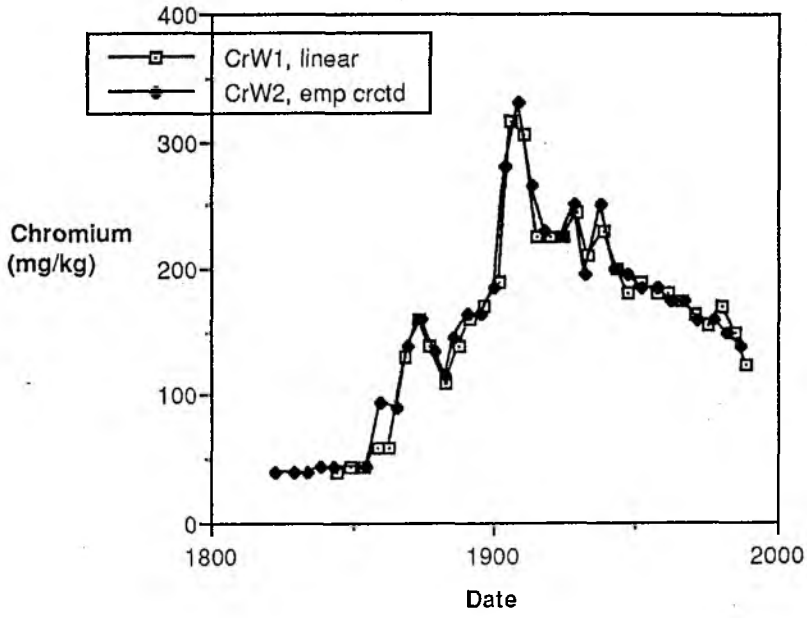

Figure 7-3 **Chromium in Replicate Cores, Widnes, with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

7.1.4 The history of Copper contamination of the Mersey Estuary

Copper concentrations (see Figure 7-4) were starting to increase slowly in the first half of the 19th century with the rate of increase speeding up towards 1890 with a period of relative stability through 1900 followed by another major increase to a peak coinciding with World War I although there was then a subsequent rapid decline before another peak in concentration with World War II. This was followed by a smaller peak in the 1950s from which there was rapid decline through to 1990 when the surface concentration was little more than 2x the pre-industrial one.

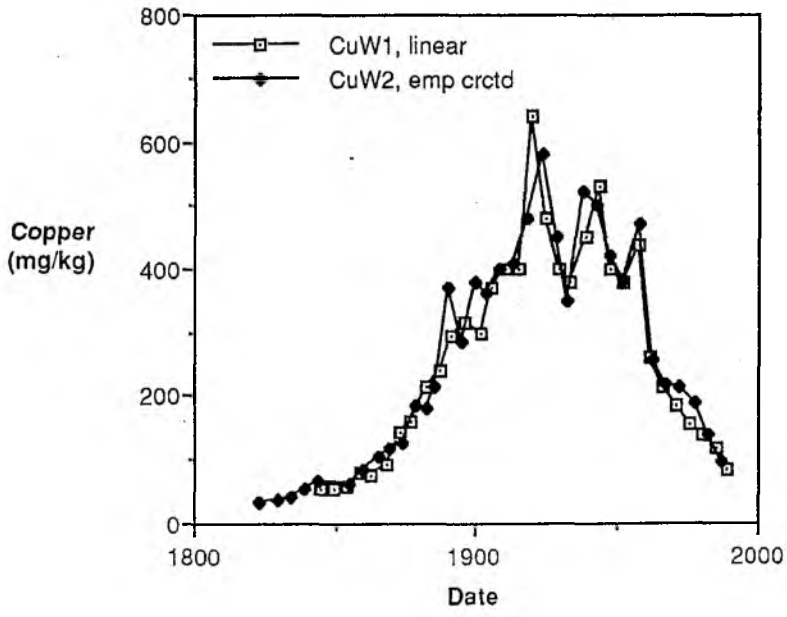

Figure 7-4 **Copper in Replicate Cores, Widnes, with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

7.1.5 The history of Mercury contamination of the Mersey Estuary

There was only a slow increase in Mercury concentration (see Figure 7-5) through the early 19th century until around 1875 when the rate increased. A subsidiary peak in concentration of >4 mg kg^{-1} was reached just before the end of the century which was then followed by a peak of 6.0 mg kg^{-1} up to World War I . A maximum concentration of between 7 & 8.0 mg kg^{-1} was reached during World War II. After a short period of decline concentrations again increased to over 6.0 mg kg^{-1} by the early 1970s although there has then been a rapid decline through to 1990. Despite the rapid decrease, concentrations at the surface remain very much higher than before the period of industrialisation.

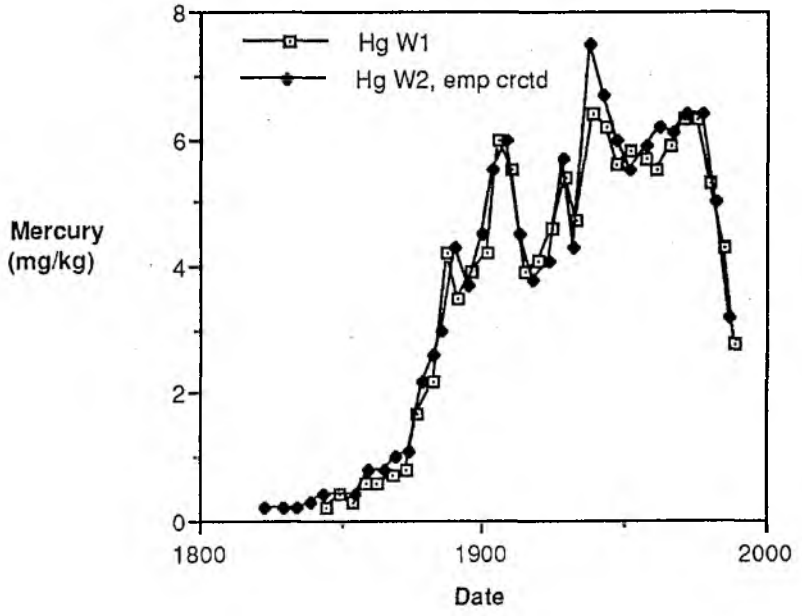

Figure 7-5 Mercury in Replicate Cores, Widnes, with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1

7.1.6 The history of Zinc contamination of the Mersey Estuary

There was a slow increase in zinc concentrations (see Figure 7-6) through the early part of the 19th century increasing at a very rapid rate from the 1880s through until World War I with a maximum of >2,500 mg kg^{-1} being reached around 1925. This was followed by a rapid decline, interrupted by a much smaller peak just after World War II. There has been a subsequent continuous decline to the surface of the core around 1990. The concentrations of around 450 mg kg^{-1} are still significantly higher than the pre-industrial baseline.

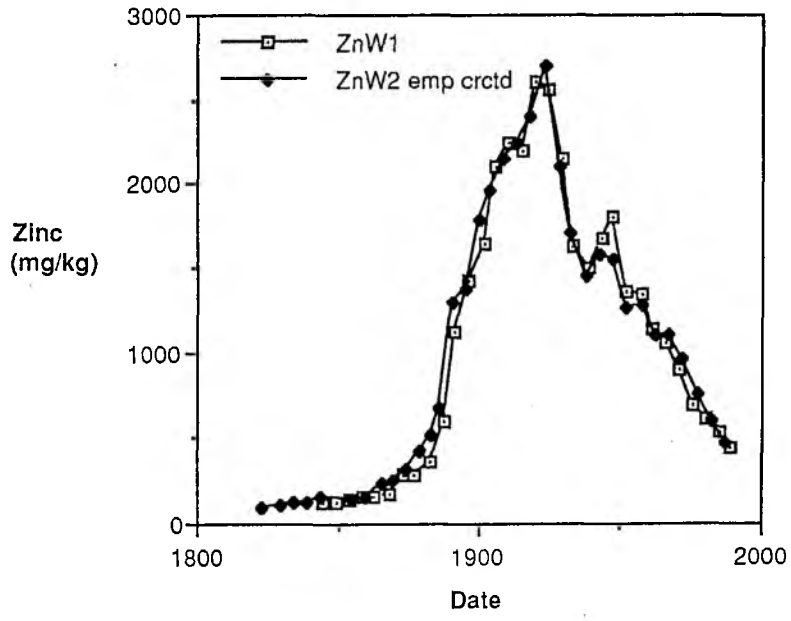

Figure 7-6 **Zinc in Replicate Cores, Widnes Warth, with empirically corrected dates to Core 2 based on the pattern of Pb in CoreW1**

7.2 Spatial distribution of metal contamination in the Mersey Estuary

Two sets of cores were taken from opposite sides of the Mersey Estuary (at Widnes Warth and Ince Marsh). This provides a very restricted view of the contamination of the estuary but it is possible to draw a limited number of conclusions.

The pattern of contamination by Mercury at Ince marsh is very similar to that at Widnes (see Figure 7-7) as are the absolute concentrations. During the 1940s and 50s, the concentrations at Ince appear to have fluctuated more than concentrations at Widnes but since the 1970s, the pattern of declining concentration has been extremely similar.

It is possible to conclude from this that the population of particles depositing at both sites are very similar in terms of their mercury contamination, particularly so after the early 1970s when it is known that the inputs of mercury were being reduced.

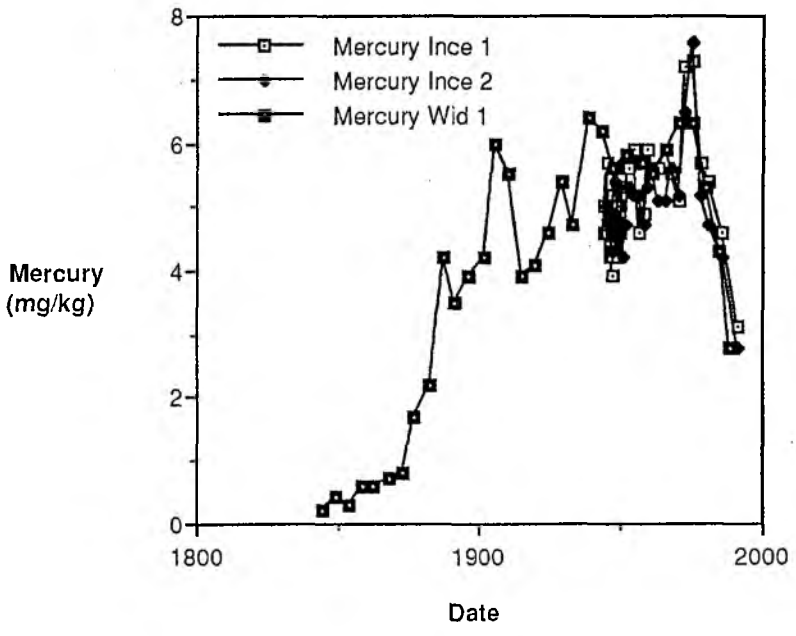

Figure 7-7 Comparison of Mercury in dated Mersey cores from Ince and Widnes marshes

A very similar picture to that for mercury is presented by data for Arsenic (see Figure 7-8) although the majority of the decline in Arsenic concentration had occurred before the base of the cores from Ince marsh. This suggests that for the period since 1945, the population of particles sedimenting at the two sites were essentially identical in terms of their Arsenic contamination.

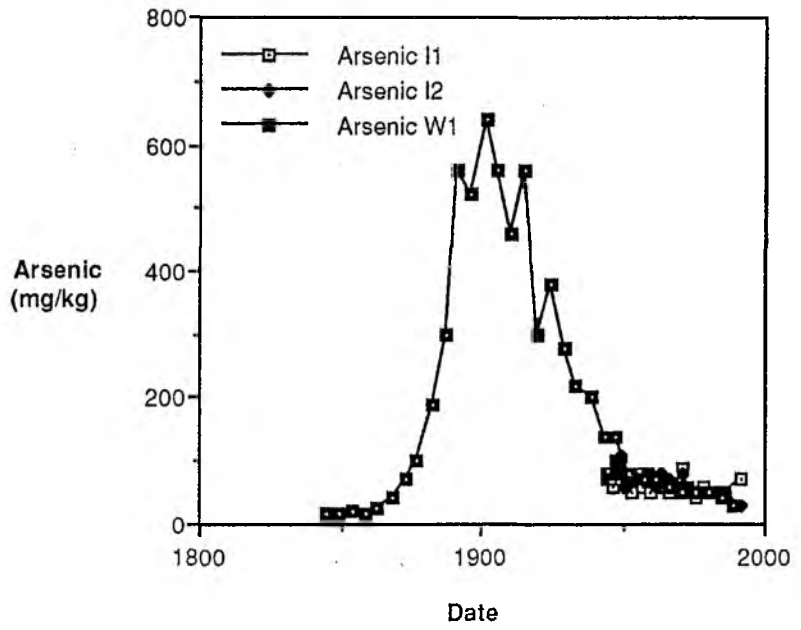

Figure 7-8 Comparison of Arsenic in dated Mersey cores from Ince and Widnes marshes

The chromium data (see Figure 7-9) show that through the 1940s and 1950s, the sediment depositing at Ince was less contaminated than that depositing at Widnes Warth although concentrations at Ince were slowly increasing to match those at Widnes. By the 1970s when concentrations at Widnes were starting to decrease, the chromium concentrations of the two populations of particles were essentially identical.

This suggests that the source of chromium could well have been in the Widnes region, resulting in a concentration gradient from Widnes to Ince. As inputs decreased, the burden locked in sediments became a factor of increasing importance until it dominated the situation. At that point, the particles throughout this part of the estuary become essentially similar in contamination terms.

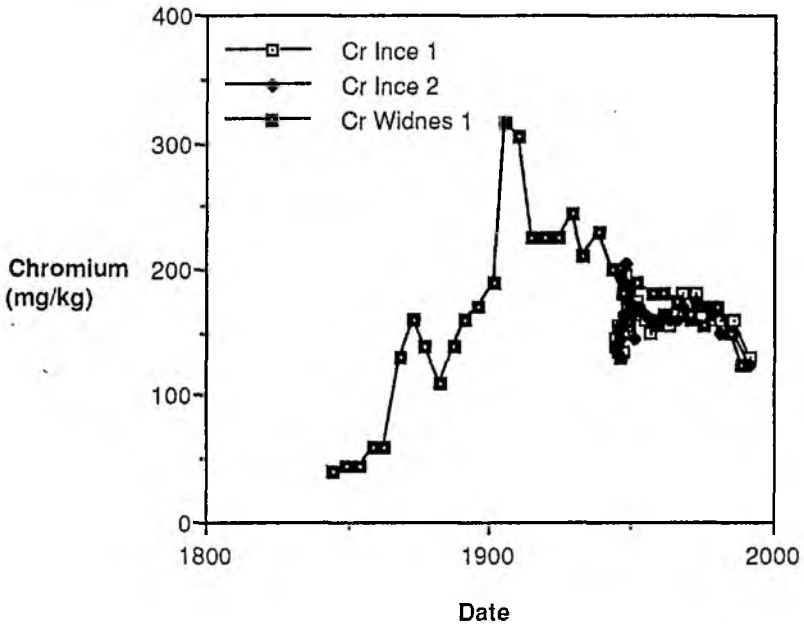

Figure 7-9 Comparison of Chromium in dated Mersey cores from Ince and Widnes marshes

An even more marked example of this phenomenon is shown by the lead data (see Figure 7-10) and the zinc data (see Figure 7-11) where the concentration at Ince was relatively stable through the 1950s and 1960s whilst the concentrations at Widnes were rapidly decreasing from a much higher level. Once the two concentrations had become the same, they both declined at the same rate.

Interestingly, the World War II sub maxima for both elements is imprinted on the pattern at Ince as well as at Widnes Warth Marsh.

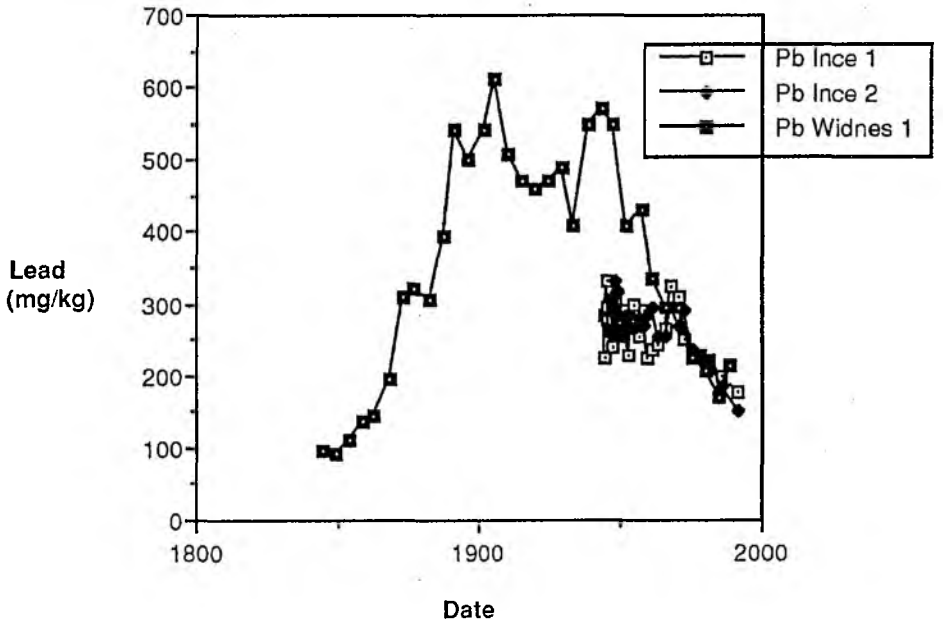

Figure 7-10 Comparison of Lead in dated Mersey cores from Ince and Widnes marshes

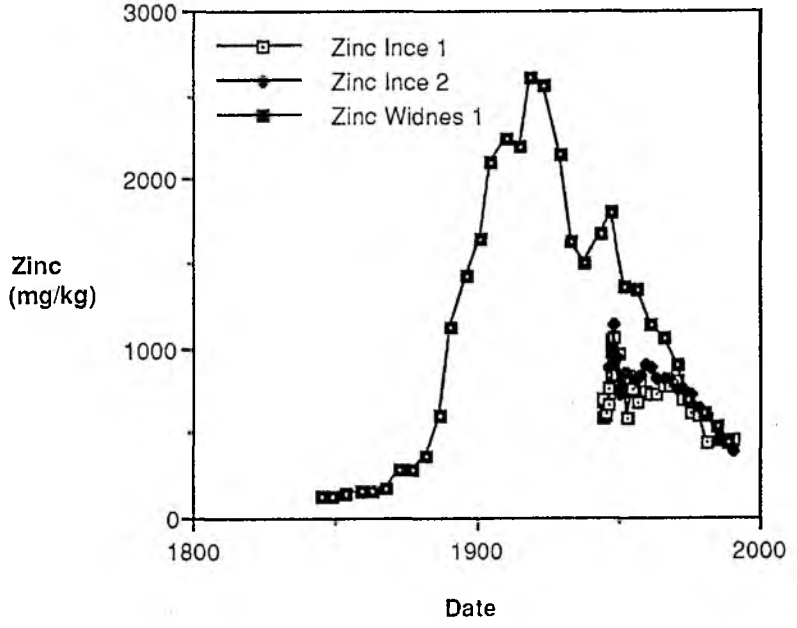

Figure 7-11 Comparison of Zinc in dated Mersey cores from Ince and Widnes marshes

7.3 Conclusions on the metal contamination of the Mersey Estuary

A very clear picture of the metal contamination of the Mersey Estuary is provided by the metals contained in sediment cores.

It is very clear that there are connections in the history shown at different locations but the level of contamination shown is site specific and related to the conditions pertaining at the individual location.

It is very desirable to reconstruct the history of contamination using a number of cores from a number of different locations.

Some of the internal processes within the estuary of movement and cleaning up of sediments are revealed. After external loadings have been reduced, the internal loading becomes important, producing a population of contaminated particles which are uniformly distributed throughout large sections of the estuary.

This allows the conclusion to be drawn that for all of the metals studied, that although historical concentrations have been very high, they have been declining for many years and that whilst estuarine processes remain as they are, they will continue to decline towards pre-industrial levels.

Arsenic is the only element which is now back very close to pre-industrial levels. This situation has been achieved because the reduction in Arsenic dispersal occurred rapidly and early in this century, probably for industrial reasons.

8. The revealed history of contamination by heavy metals in the Ribble Estuary

The picture of metals contamination in the Ribble Estuary developed from the sediment cores is clear although not as dramatic as in the Mersey (see Figure 8-1 to Figure 8-5). However, each of the dated profiles shows one feature which may be an artifact induced by the sediment type present in the core which is illustrated by the Loss on Ignition data (see Figure 6-3). The last few slices at the bottom of the cores from Banks Marsh were described by Murdock as very sandy, a fact which is borne out by the very low organic matter suggested by the LOI data (see Section 6.2). Since most of the pollutants studied will become preferentially associated with fine organic rich particles, the early rapid increase in pollutant concentration in the cores is probably the result of this effect. However, the subsequent increase in concentration with time probably accurately reflects the increasing level of environmental contamination.

The concentration of chromium in the Banks Marsh cores (Figure 8-1) has steadily increased from the 1930s through until around 1980 after which there has been a modest decline.

Copper increased in concentration until around 1970 (Figure 8-2) but after which there has been a steady decline which accelerates towards the surface. However, surface concentrations remain well above the pre-industrial baseline.

Mercury increased in concentration at a steady rate until around 1960 when there was a rapid increase to peak concentrations of around 2.5 mg kg^{-1} which were maintained through the early 1970s. Since the mid 1970s there has been an increasingly rapid decline in concentrations although surface mercury concentrations are still considerably elevated above the baseline.

Lead (see Figure 8-4) has shown a slow increase from 1930 through until 1970 after which there has been a decline.

Zinc (see Figure 8-5) shows a similar pattern to lead.

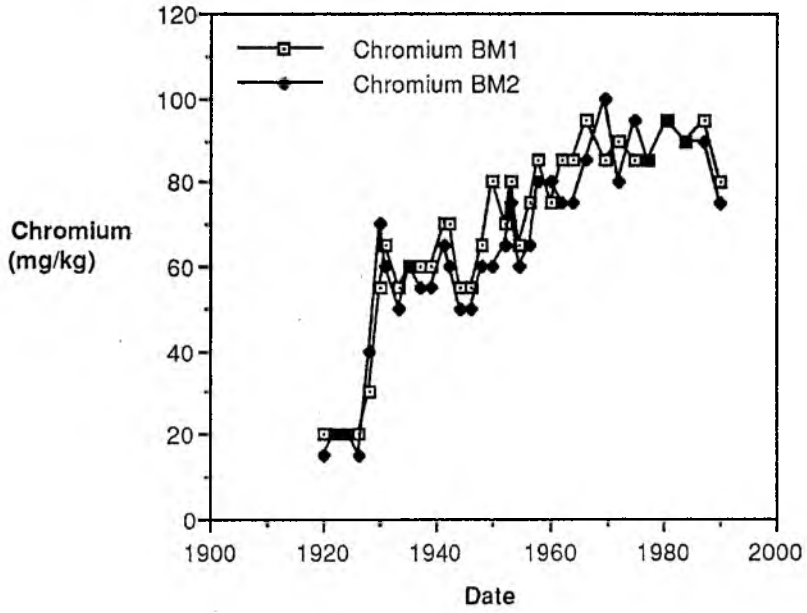

Figure 8-1 Contamination of the Ribble estuary by Chromium

NOTE: Dates derived using 'Final Dating Scheme' from this Report

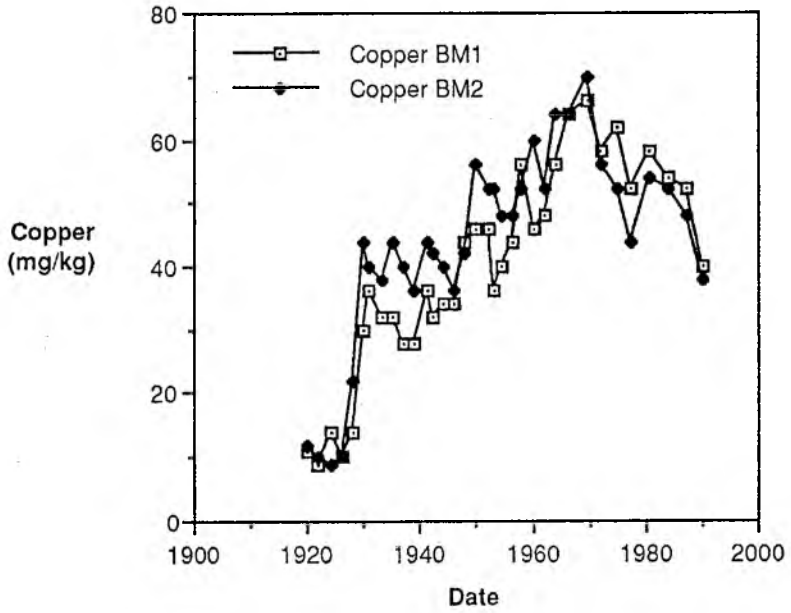

Figure 8-2 Contamination of the Ribble estuary by Copper

NOTE: Dates derived using 'Final Dating Scheme' from this Report

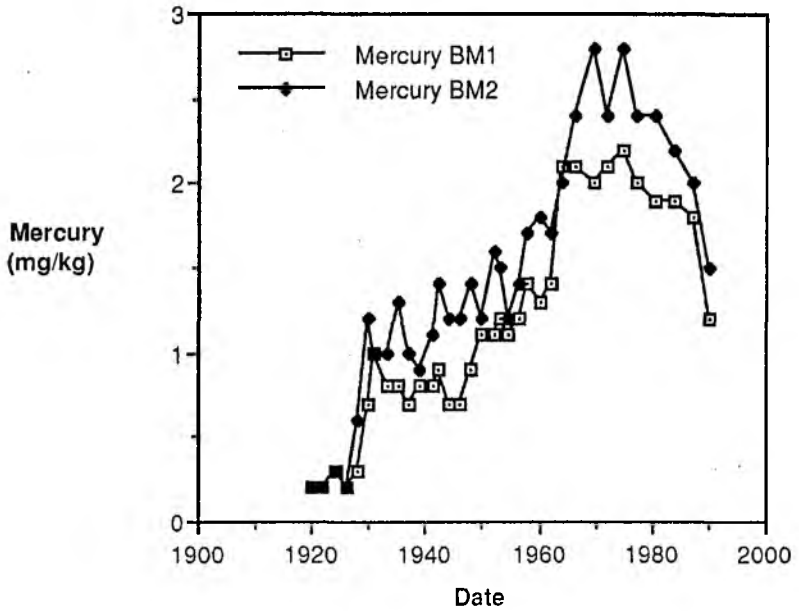

Figure 8-3 Contamination of the Ribble estuary by Mercury

NOTE: Dates derived using 'Final Dating Scheme' from this Report

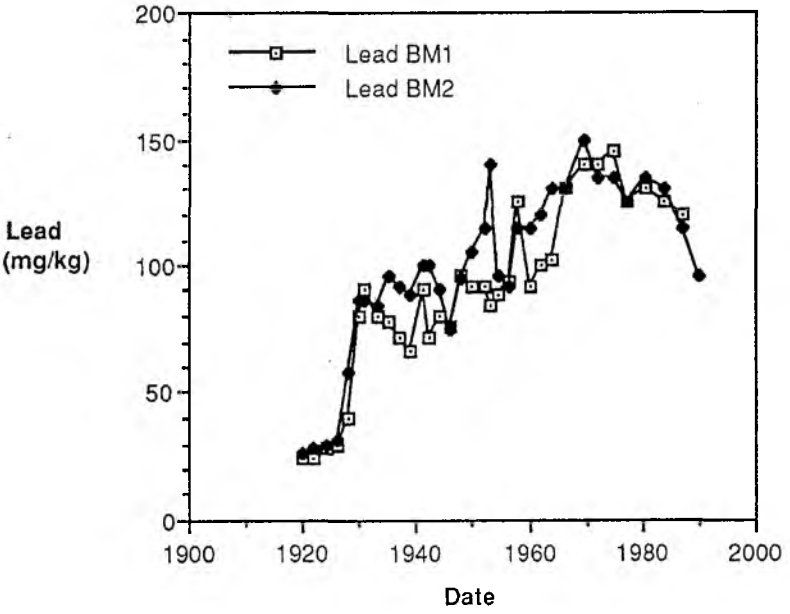

Figure 8-4 Contamination of the Ribble estuary by Lead

NOTE: Dates derived using 'Final Dating Scheme' from this Report

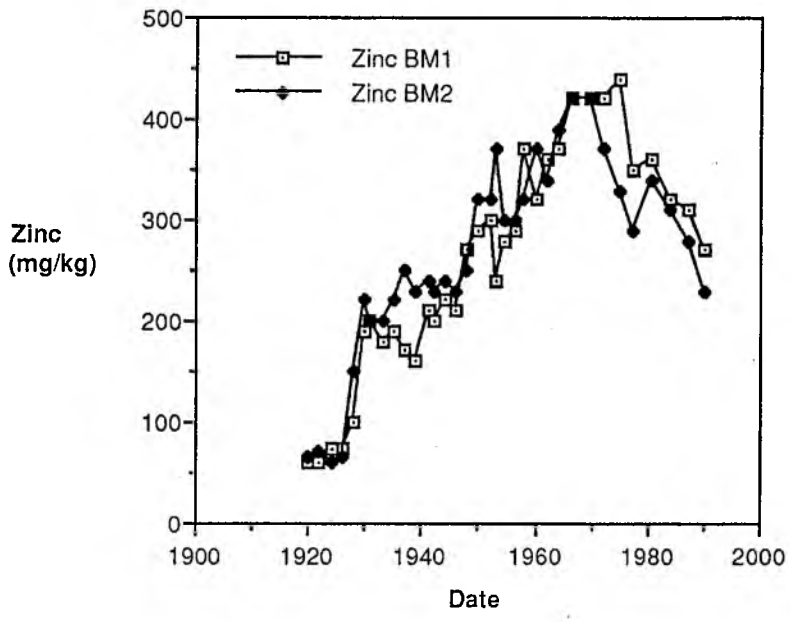

Figure 8-5 Contamination of the Ribble estuary by Zinc

NOTE: Dates derived using 'Final Dating Scheme' from this Report

9. The Revealed history of contamination by organochlorines in the Mersey estuary

9.1.1 Contamination of the Mersey Estuary by DDT and related chemicals

Probably the most obvious feature of the organochlorine content of the cores analysed in this study is the remarkably sharp increase in DDT concentrations (eg see Figure 9-1) from very low concentrations to amounts which are very high, even on a global scale. It is more remarkable that this increase occurs over a very short period of time, which in the case of one Widnes core is represented by only one core slice.

The pattern of increase in DDT in the Mersey, where absolute ΣDDT concentrations are very high is also reflected in the Banks Marsh cores (see Figure 10-1) although concentrations there are much lower than in the Mersey (<100 $\mu g\ kg^{-1}$). The patterns of increase and subsequent decrease are very similar at both Mersey locations sampled (see Figure 9-2) although there could not be complete replication in the samples analysed for Ince Marsh because of cost limitations.

It is important to consider the factors which have produced such a remarkably clear signal in the sedimentary record of the area for comparison with the history of other organic chemicals with much more gradual changes in concentration.

The working hypothesis is that the River Mersey system was rapidly and comprehensively contaminated by DDT group compounds from a manufacturing facility located in the Mersey catchment area and the majority of the observed contamination has not arisen from widely dispersed uses of the product as an insecticide. Since the contamination arose from the manufacture of DDT during World War II which was the first widespread use of the material, the DDT in these cores was likely to be the earliest occurrence of widespread DDT contamination anywhere in the world and has probably remained unnoticed until the present day. The detailed facts behind these assertions are discussed below. However, when comparisons are made with other organic compounds in the sedimentary record and at other locations, it is important not to forget that the way in which the DDT contamination of the sediments has arisen in this estuary is probably unique to the Mersey and to this particular group of compounds.

The very rapid increase in sedimentary DDT concentrations was almost certainly brought about by the way that DDT has reached the Mersey estuarine environment. DDT was considered to be a strategic chemical during World War II because of its importance in controlling the insect vectors of disease amongst troops and displaced persons in Europe and other theatres of war. Manchester, on the banks of the River Mersey was the first location anywhere in the world chosen to put DDT into full scale manufacture.

DDT was discovered in 1874 but its remarkable insecticidal properties were not realised and developed until much later during the late 1930s by Paul H. Müller. By 1942, when DDT had been tested and used in Switzerland, there was no doubt that it was, potentially of tremendous importance to military medicine and hygiene in time of war. Switzerland was a neutral country, but arranged to inform the diplomatic representatives of the various belligerent Powers of their work with DDT. At roughly the same time, J.R. Geigy S.A. of Basel took out a British Patent (No 547871, 1942) with similar action in Germany and the USA.

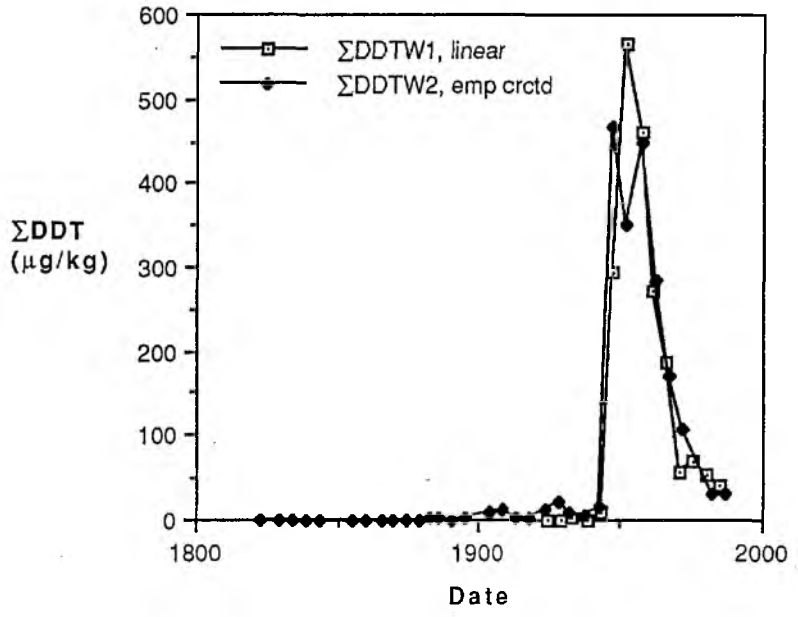

Figure 9-1 Profiles of ΣDDT in Widnes Warth, Cores W1 & W2

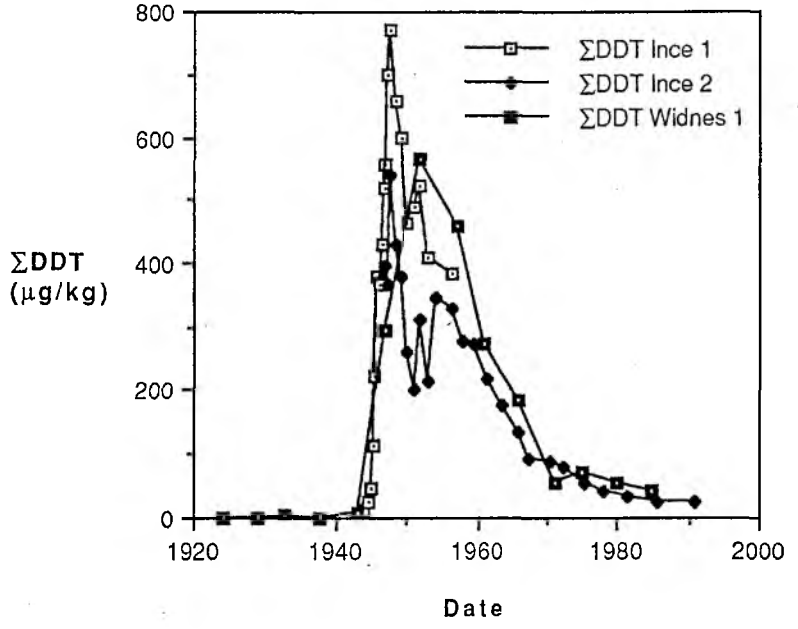

Figure 9-2 Comparison of ΣDDT in dated Mersey cores from Ince and Widnes marshes

By early 1943, British tests had confirmed the efficacy of DDT in killing lice, the main vector of Typhus, and it was decided that an all out effort to use DDT against lice would proceed. The British Government set up the Insecticidal Development Panel and the whole force of the Ministry of Production was mobilised to expedite the manufacture of the new insecticide. The Prime Minister, Winston Churchill, requested that "all Ministries concerned should urge DDT production to the utmost of their resources."

The atmosphere of how it was achieved (and the consequential likely lack of attention to niceties such as environmental protection) is best communicated by repeating a quotation from the work of West and Campbell as quoted in Mellanby (1992):

> 'The beginning of 1943 was a difficult time for British industry. Plant and labour even for essential purposes were almost unobtainable. To make the most of what was available was the order of the day, and difficulties arose at every stage. At the Ministry of Supply the powers of organisation, enthusiasm, and optimism of the chief officers of the Departments eliminated red tape and overcame the complications of supply due to the war. In Manchester, at the Trafford Park works of the Geigy company, there was a drive for the erection of plant and production of DDT. DDT at that time became a war priority of the highest order.... As early as January 1943 a few pounds of DDT of high purity were made at the Geigy Fine Chemicals at Trafford Park, and in April 1943 the first batch was produced at the pilot plant. This plant continued to produce several tons throughout the following months until the first bulk production came forward at Trafford Park in November 1943. **This was the first regular large-scale production outside Switzerland.'**

The manufacture of DDT results in the production of a number of different types of waste which can contain DDT residues but no details of these are currently available to the author. However, it is known that the 'caustic waste' stream is water based and in the United States was disposed of into storm drains and sewers (Venkatesan et.al., 1996). It seems probable that the same occurred in the UK and that this is responsible for the remarkable contamination of the River Mersey system all of the way down to the estuary and beyond. Thus the rapid increase in DDT concentrations in the cores cannot have occurred before late 1943 and is almost certainly a consequence of the switching on of large scale production in Manchester in Autumn 1943. It can be seen, that at Widnes, this date fits very closely to those predicted by the simple linear model of deposition (see Figure 6-14). The lower concentration but similar shape of the DDT profile in the Ribble cores seems to suggest that the transport of DDT by marine processes from the Mersey to the Ribble was important and probably does not reflect independent manufacture or use of DDT within the Ribble catchment area.

The ratio of the different DDT isomers changes through the contaminated part of the cores and is not even completely consistent between cores taken very close together. However, the overall concentrations of the ΣDDT are very close in replicate cores. The differing proportions of DDD and DDE isomers is possibly the result of differences in degree of oxygenation in the sediments since DDD is the anaerobic breakdown product.

The large amount of DDT compounds present in the anaerobic estuarine sediments appears to affect the ratios of the different isomers throughout the system and could be responsible for the relatively high proportions of DDD compounds (Leah 1997), present in the biota of the eastern Irish Sea, relative to the aerobic breakdown product, DDE.

It is reasonable to suppose that since the Trafford Park factory was almost certainly the only feasible source of DDT when the signal appears in the sediments it is possible to make a series of deductions about the source and fate of DDT:

In the Mersey sediments, there is the complete range of the isomeric compounds present in technical DDT as well as their environmental breakdown products (eg see Figure 9-3). The active insecticidal compound, ppDDT forms only a small proportion of the DDT chemicals measured in these cores despite normally forming approximately 80% of technical formulations (Bopp et.al., 1982).

The DDD anaerobic breakdown products form a surprisingly high proportion of the overall contamination in comparison to most situations where DDE has been the

principal breakdown product (eg 60-100% ppDDE in New Zealand soils, in Hendy & Peake, 1996). This should perhaps not be surprising, since most of the breakdown will have occurred in very anaerobic sediments within the estuary.

The proportion of opDDD is also exceptionally high, presumably reflecting a high proportion of opDDT in the original technical mixture. This may be a feature of the manufacturing process used which in its early days may have been very inefficient in producing the required ppDDT isomer.

The highest concentrations observed in the Mersey cores involved in this study (up to nearly 800 $\mu g\ kg^{-1}$ at Ince Marsh), are very high even on a global scale. Only one or two sites in the USA, involved with the manufacture of DDT have produced much higher. One area which seems to have similar contamination problems due to similar causes is the Newark Bay estuary in New Jersey, USA (see Gillis et.al., 1995 for a comprehensive report on the area). The study is not directly comaparable, but 246 sediments were analysed giving a good overview. A regional mean concentration 100-300 $\mu g\ kg^{-1}$ was measured throughout the estuary with the exception of one area, the Arthur Kill, where concentrations averaged over 700 $\mu g\ kg^{-1}$. Maximum concentrations at depth (corresponding with the period 1940-1960 was >1,500 $\mu g\ kg^{-1}$. There were 30 companies within the catchment area of Newark Bay which were involved in DDT manufacture or its formulation between 1943 and 1972 when it was banned. Earlier work on Arthur Kill surface sediments had produced remarkable concentrations up to 148,000 $\mu g\ kg^{-1}$(quoted in Gillis et.al., 1995). Gillis et.al. concluded that the DDT group compounds present in Newark Bay Estuary at the time of their survey were potentially hazardous to aquatic and avian wildlife.

The most contaminated area known outside the USA found to date was in New Zealand due to contamination from a DDT formulating factory (489 $\mu g\ kg^{-1}$, Hendy & Peake, 1996). In comparison, the maximum concentration of summed ppDDT isomers in short Thames cores was <10 $\mu g\ kg^{-1}$ (Scrimshaw & Lester, 1995).

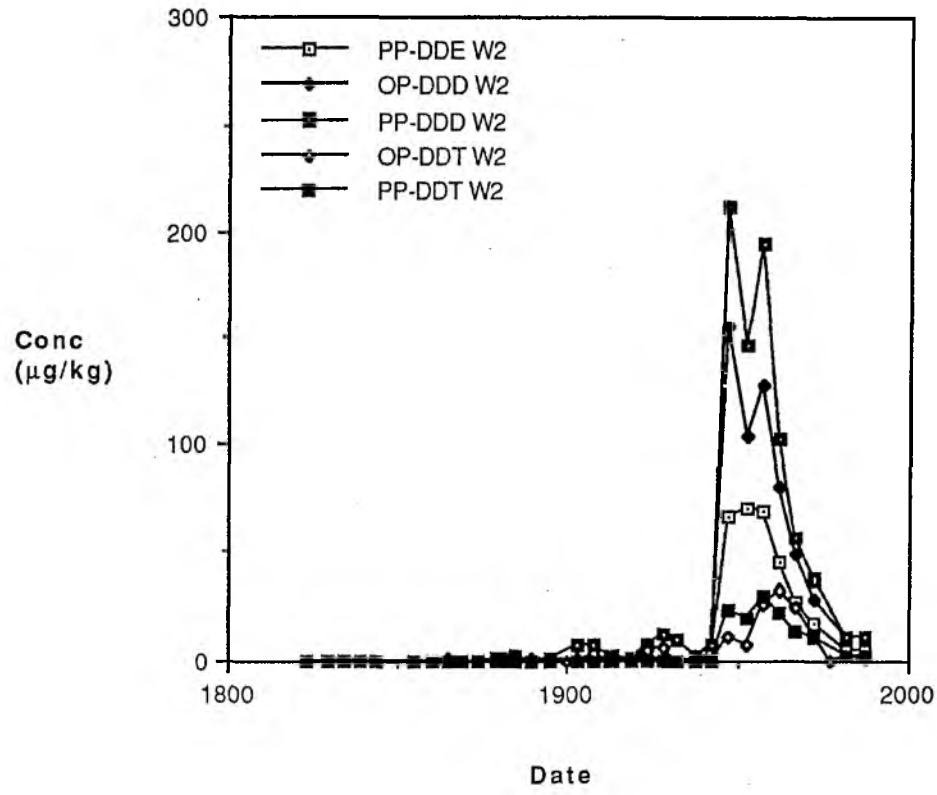

Figure 9-3 **The profiles of DDT group chemicals in Widnes Warth Core W2**

9.1.2 Contamination of the Mersey Estuary by PCBs

The picture of contamination produced by data for Arochlor1254 or by the summed group of ICES7 congeners (#28, 52, 101, 118, 138, 153, 180) is extremely similar (cf. Figure 9-4 & Figure 9-5). Since the quantity ΣICES7 is much more reproducible and can be measured with a higher degree of accuracy, the further discussion of PCB contamination will use only ICES7 results. This ignores certain subtle changes in the congener composition of the contamination which it is now known occur in the sediments. Some initial comments on this are included in section 9.1.3 although the large body of data which is available needs to be analysed in more detail and will be reported elsewhere.

PCBs were introduced into industrial uses in the 1930s and became increasingly popular. They were not discovered to be environmental contaminants until 1966 by Jensen in Sweden. A ban on new uses in the USA was introduced in 1979 with a complete ban in the USA following in 1984. Commercial manufacture did not start in the UK until 1954 although up to 100 tonnes was imported prior to this date. Peak production in the UK was between 1965 & 1975 (Gevao et al., 1997). Production in the UK was discontinued in 1977.

Contamination in the Mersey sediments does not appear until the 1940s, rapidly rising to a peak around 1970 (see Figure 9-4 to Figure 9-6). Since then there has been a consistent decline to the surface which however remains much higher than expected background levels.

Contamination levels at both Widnes and Ince are remarkably similar, suggesting that the population of particles sedimenting at both sites were essentially the same in terms of contamination level. Depending on the accuracy of dating of the sediments, there is slight evidence that there was a lag in maximum concentration at Ince (taking into account both the differences and similarities in the heavy metal patterns).

Taking into account the industrial history of manufacture and usage of PCBs summarised above, it seems likely that the contamination of the Mersey system is probably due to primary industrial usage, with peak levels declining immediately industrial use began to decline. This set of circumstances is likely to be different from sites more remote from industrial activity where the contamination must be due to long-range transport from contaminated sites. For example, in a study of sediments in Esthwaite Water, the peak in sediment concentration corresponded to 1979 (±2) (Gevao et.al., 1997)

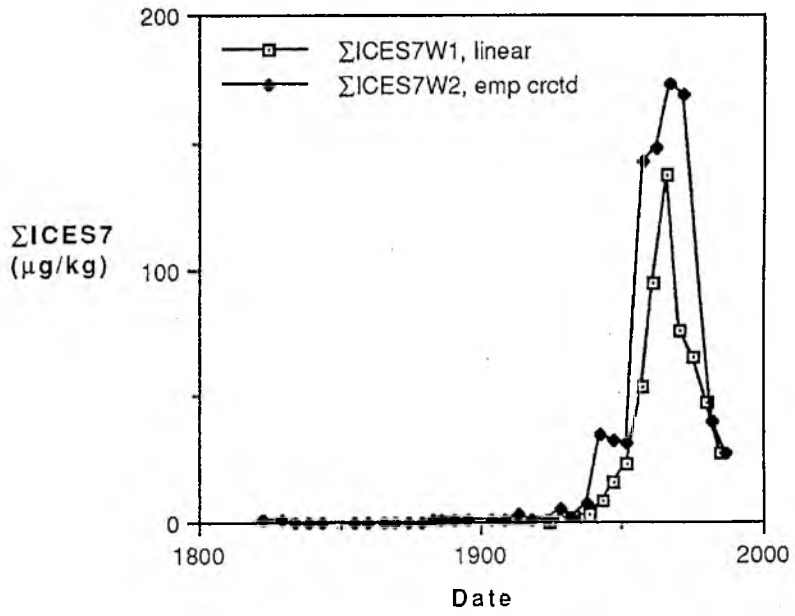

Figure 9-4 Profiles of ΣICES7 in Widnes Warth, Cores W1 & W2

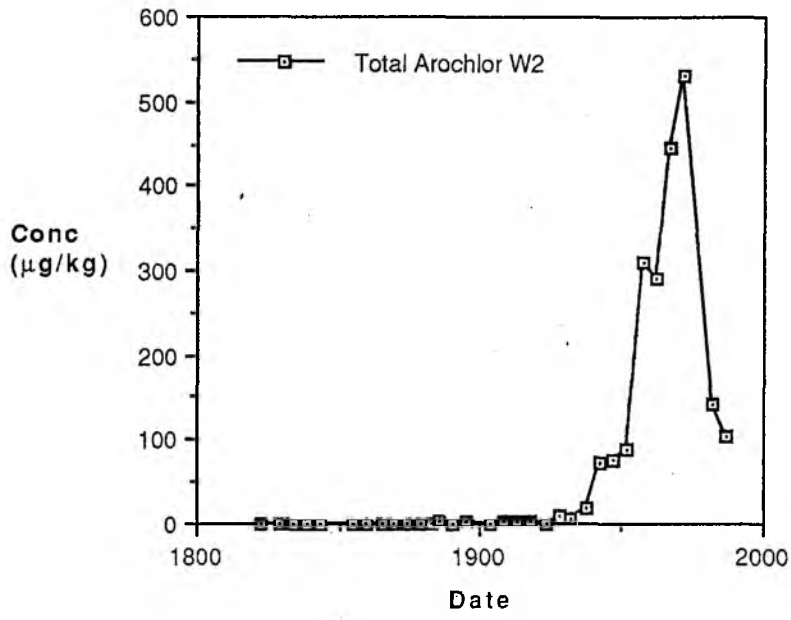

Figure 9-5 Profile of Arochlor 1254 in Widnes Warth, Core W2

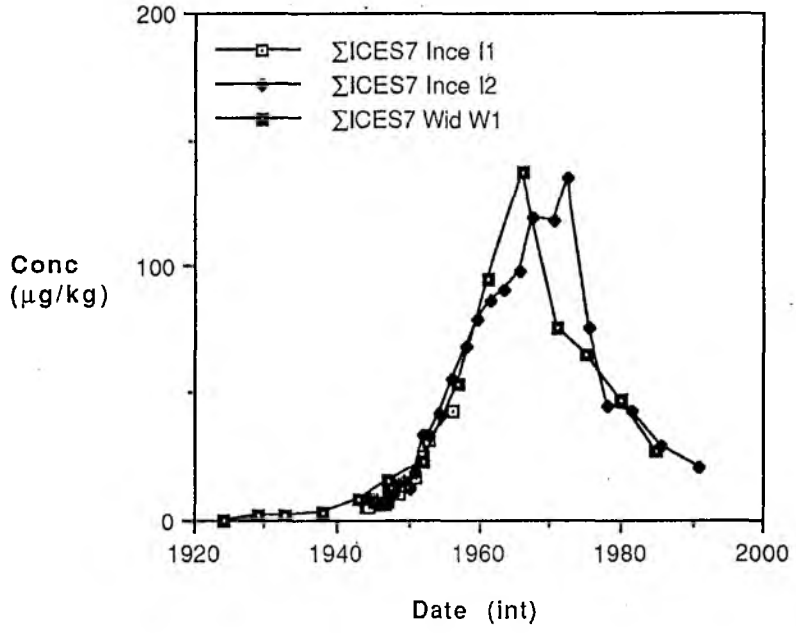

Figure 9-6 Comparison of PCBs (as ΣICES7) in dated Mersey cores from Ince and Widnes marshes

It would be expected that the PCB concentrations found in a large area such as the Mersey estuary will be lower than in a confined space such as the freshwater part of a river because of the massive dilution after discharge provided by tidal flows. However, the concentrations found during this study are high, both on a local and a global scale. A comparison of the contamination revealed in the Mersey with that found elsewhere is given below.

Following the Piper Alpha incident in 1988, Wells et al. (1989) defined a series of (arbitrary) concentration guidelines (on a dry mass basis) for the categorisation of concentrations of PCBs in sediments:

<0.2 μg kg^{-1}	Contamination not detectable
0.20 - 20 μg kg^{-1}	slightly contaminated
21 - 100 μg kg^{-1}	contaminated
>100 μg kg^{-1}	heavily contaminated

The PCB data from the Mersey cores reveals the gradual build-up to peak concentrations in the late 1960s with a gradual improvement since then although concentrations remain fairly high.

The concentrations found in surface sediments in the estuary during this study (c.35 μg kg^{-1} ΣICES7, c.530 μg kg^{-1} ΣPCB_{A1254}, 400 μg kg^{-1} $\Sigma PCB_{1:1:1}$) are comparatively high compared to the marine sediments found further offshore. The highest concentrations found in surface marine sediments in a recent study (Camacho-Ibar & McEvoy, 1996) in Liverpool Bay were from the Burbo Bight area just off the mouth of the Mersey (less than 38μg kg^{-1} ΣPCB) in an area of relatively organic rich sediment (1.17% TOC) and fine sediment. Camacho-Ibar & McEvoy, (op.cit.) showed a strong relationship between fine particles and PCB concentration. Further afield in the Irish Sea, in another recent study, the range was between 0.2 -42 μg kg^{-1} ΣPCB (Thompson et. al., 1996). In a recent survey, of fine surficial sediments from Cardigan Bay, most were <10 μg kg^{-1} ΣPCB (ICES) (Jones & Franklin, 1997). Just one contaminated site in the harbour at Aberystwyth contained concentrations of 191 μg kg^{-1} ΣPCB(ICES). The maximum concentrations in the estuary of the River Thames were 132 μg kg^{-1} ΣPCB(ICES) (Jones & Franklin, 1997). PCB contamination (as A1248) averaged only 14 μg kg^{-1} in mud flat sediments along the Thames (Scrimshaw & Lester, 1995), which was essentially similar to general levels in the Humber area (Klamer & Fomsgaard, 1993), the Rhine (Klamer & Laane, 1990), and the Scheldt (Delbeek et.al., 1990).

Thus, surface sediments in the Mersey Estuary are more contaminated than marine sediments throughout a large part of the Irish Sea (although part of the differential could be related to the high organic and fine particle content present in saltmarsh sediments) and other similar estuarine areas in the North Sea. However, they are much less contaminated than the fine suspended sediments in the Hudson River, New York (with which they should be comparable in terms of general properties) which averaged >1,000 μg kg^{-1} (Achman et.al., 1996) or various areas of Newark Bay Estuary, New Jersey (Ianuzzi et.al., 1995).

The dumping of contaminated sewage sludge is one major alternative potential source of PCB in maritime areas and with a major dumpsite outside the mouth of the Mersey Estuary could be one possible source for PCB to contaminate the sediments. Once such sludge has been released into the sea, it would be expected that the contained PCB would become entrained in seabed sediments near to the dumpsite or possibly further away, depending on the hydrology. Such sediments could conceivably enter the Mersey estuary and accumulate in salt marshes. However, Alcock and Jones (1993) recently reported a mean of 292 μg kg^{-1} Total PCB in sludge from 12 sewage works from North West England. This is less than the current surface contamination levels within the Mersey estuary and thus unlikely to be the source of contamination.

At the sludge dumpsite at Garroch Head off the Clyde, Kelly (1995) measured 210 - 410 μg kg^{-1} ΣPCB for the 35 congeners quantified in that particular study, (463 - 900 μg kg^{-1} ΣPCB_{A1254}) compared to less than one tenth of this at the remote comparison site, Pladda Head. Levels at Garroch Head have decreased in recent years but in 1988

they were similar to those at the New York Bight sludge disposal ground where 2,200 $\mu g\ kg^{-1}$ ΣPCB_{A1254} was measured in 1975 (West and Hatcher, 1980). In comparison, the highest concentrations recently found in short, undated estuarine sediment cores from Hoolpool Gutter in the Mersey Estuary were 3,100 $\mu g\ kg^{-1}$ $\Sigma PCB_{1:1:1}$ (Leah, 1997b)

The PCB concentrations found in the Mersey are likely to be above the equilibrium concentration with the overlying water (cf. Achman et.al., 1996) so that they will be acting as a source of PCB to the biota (cf. Bremle & Larsson, 1997 & Bremle et.al., 1995).

The main conclusion concerning PCB contamination is that the Mersey contains some very PCB contaminated sediments.

Overall, the estuarine sediments remain relatively highly contaminated, despite these concentrations having declined in recent years.

It seems improbable that PCB contamination dumped on the sewage sludge site outside the Mersey estuary could be responsible for producing the elevated levels in the estuarine sediments, particularly the high concentrations deeper in the sediment profile. It is concluded that sources within the estuary are most likely to be responsible for the contamination of the system.

It is possible to conclude with confidence that there has been a major decrease in the PCB contamination of the surface sediments in the Mersey estuary through the last twenty years, although surface levels are still relatively high in comparison with more remote areas.

9.1.3 Changes in PCB congeners composition through time

The individual concentrations for the ICES7 congeners are plotted for Widnes Warth, core W2 in Figure 9-7. Even if the change in the early 1950s is ignored, it can be seen that there have been major changes in PCB congener composition through the period 1950 - 1980. This is shown very clearly for a small group of congeners in Figure 9-8 for Ince Core I2. The shifts seem to correspond with a change in the composition of the contaminating mixture rather than changes due to weathering or differential mobilisation which have been postulated elsewhere as the cause of change.

There does not seem to be a consensus in the literature. For example, Oliver et.al., (1989) found a shift to less chlorinated congeners with time for cores in Lake Ontario which was attributed to a change in production to lower chlorinated PCBs (Arochlor 1016).

Differential degradation of PCBs (Farley et.al., 1994) was found to be unlikely to account for changes in the congener pattern in Großer Arbersee sediment cores (Bruckmeier et.al., 1997) as there was no decrease in the higher chlorinated congeners with depth which would be required if dehalogenation was a major factor.

Their rationale was :
"Post-depositional re-mobilisation could not explain the profiles found in the Großer Arbensee. Enrichment of the low chlorinated congeners would have been expected in the upper sediment layers because they volatilise more easily than higher chlorinated congeners. However, the top horizon (1991-3) contained less #28 and #52 than the sediment layers deposited in 1985-91 and 1981-1985 suggesting that the profile reflects the true deposition pattern. " (Bruckmeier et.al., 1997)

Gevao et.al., (1997) concluded that there was some evidence of mobility both upwards and downwards in cores from Esthwaite Water although the concentrations of PCBs (derived from atmospheric inputs) were much lower than are being considered here.

Axelman et.al., (1995) found that in the Baltic Proper, PCB composition was constant through time, although PAH composition changed.

Beurskens et.al., (1993) dated cores by using radioactive Caesium together with characters formed during the physical alterations of the area including the formation of a freshwater lake. They were able to resample the same locations at some stage later and concluded that some PCB had disappeared between the two samplings. However, in view of the likelihood of small differences in deposition arising over very small distances, such an argument is not sustainable because the original sampling location was only approximated on the second occasion.

Overall, it seems that PCB composition can remain fairly constant through time in sediments, suggesting that where gross changes in composition occur such as in the Mersey, these are due to changing composition of the materials entering.

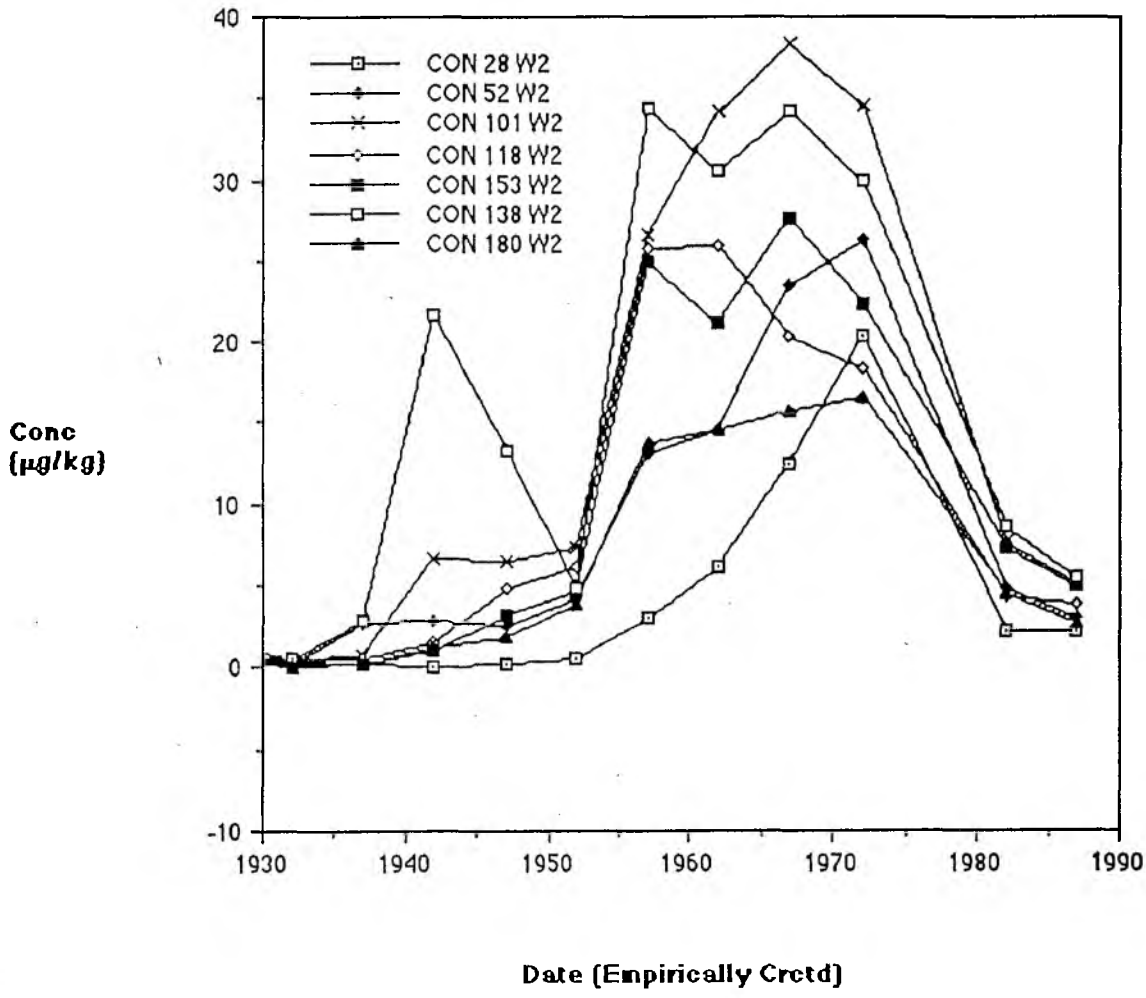

Figure 9-7 Profiles of PCB congeners in Core W2 from Widnes Warth

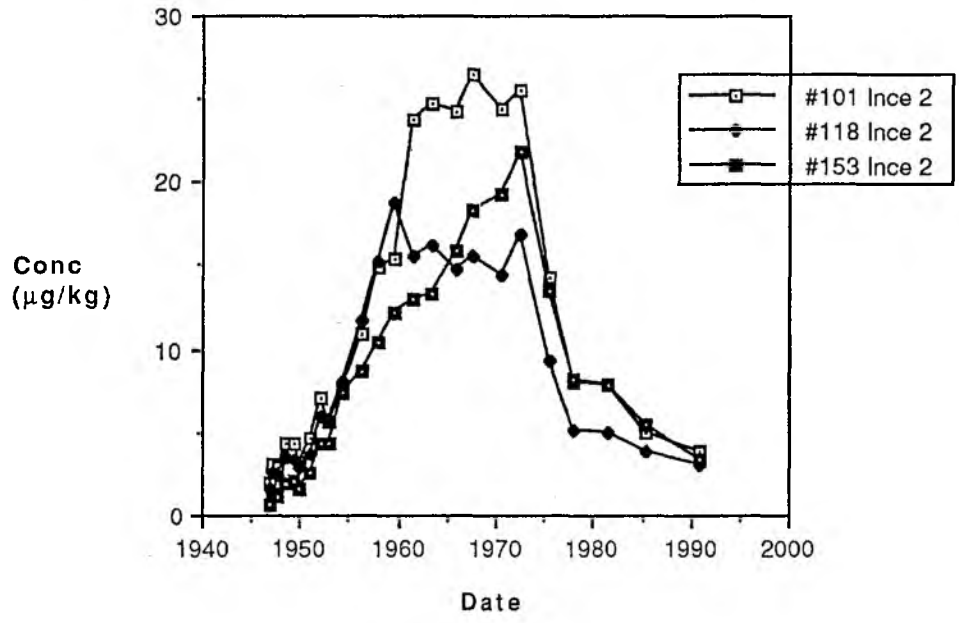

Figure 9-8 Profiles of PCB congeners in Core I2 from Ince

9.1.4 Contamination of the Mersey Estuary by Dieldrin

The 'drins' (aldrin, isodrin, endrin and dieldrin) belong to the chemical family of chlorinated cyclodienes and were widely used in the UK as contact insecticides from the 1950's with a decline in use since the 1970's. These are amongst the most toxic and persistent of all pesticides. Aldrin and dieldrin are stereochemically related, aldrin being rapidly metabolised to a form of dieldrin. Endrin is a stereoisomer of dieldrin and Isodrin is an isomer of aldrin. Chlordane is chemically related to the 'drins' and in technical form is a mixture of variously chlorinated dicyclopentadienes.

The data available for Dieldrin in sediment samples have been severely restricted by analytical difficulties. It did not prove possible to apply a standard clean-up method to Mersey samples because of problems with a complex set of interferences. Despite major effort being put into development of an alternative multi-residue extraction and clean-up scheme, it did not prove possible to include Dieldrin in the standard group of determinands without losing other major compounds. As a consequence, only a small number of samples from Widnes Warth core W2 were analysed. The extracts were fractionated just for Dieldrin.

On the basis of these results (Figure 9-9) it can be seen that there is a peak of Dieldrin in the sediments of >1.0 µg kg^{-1} which centres on 1960, a pattern which fits with the expected usage of the compound. This concentration is relatively low compared to areas such as New Zealand where there was perhaps more intensive usage of the pesticide (eg Hendy & Peake, 1996). However, because of the low number of data, not too much significance should be attached to the presence of small amounts of Dieldrin in a small number of earlier samples. Despite the analytical difficulties, we are confident that there are **not** significant quantities of Dieldrin in surface samples.

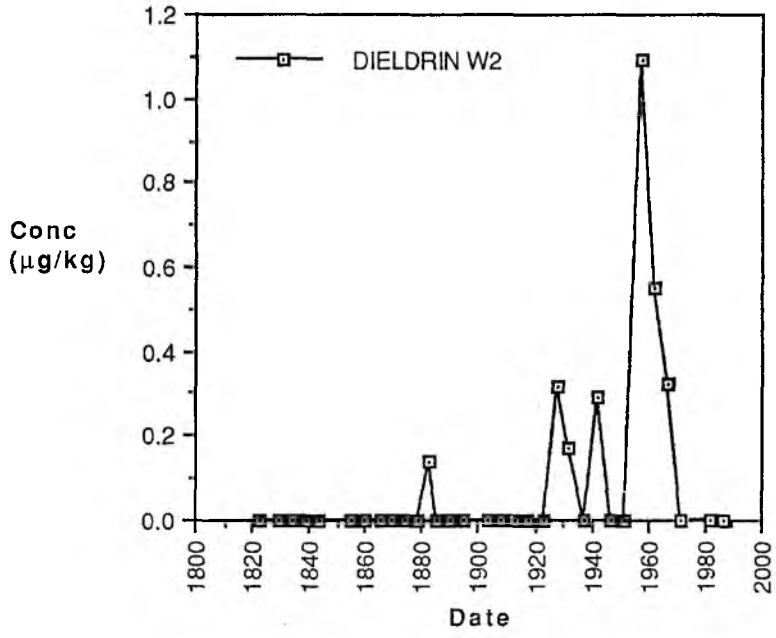

Figure 9-9 Profile of Dieldrin in Widnes Warth, Core W2

9.1.5 Contamination of the Mersey Estuary by HCB

The Chlorobenzenes are a group of ubiquitous materials which are produced in large quantities by industry, both on purpose and as unintentional by-products. The US National Academy of Sciences recommended (in 1975) that increased attention be paid to hexachlorobenzene because of its detection in many marine samples, its persistence, and its high toxicity (Murray and Beck, 1989). Hexachlorobenzene has been used as a seed fungicide and wood preservative. It is strongly sorbed to sediments and suspended solids (Howard, 1989).

Hexachlorobenzene is the only major chlorinated hydrocarbon positively identified in this study which is present in significant amounts early in this century (Figure 9-10). The rise in concentration started in the 1880s rising to a peak concentration of >20.0 µg kg^{-1} more or less coincident with World War I. A decline is then followed by a second peak coincident with World War II. It is interesting to note (Figure 9-11) that in contrast with many of the other chlorinated compounds in this study, there is a significant discrepancy between the concentration in Ince sediments and Widnes in the period around 1940. The concentrations at Widnes were in decline but were still increasing at Ince until around 1950 when they became very similar. After a fluctuation, which is evident at both locations, they then decline towards the surface.

At this stage, it is not possible to assess the significance of the presence of small amounts of HCB at the bottom of the core.

Not very much information is available on worldwide production history for HCB (Van Zoest & Van Eck, 1993) but peak concentrations in sediment cores were determined to be in layers deposited between 1965 and 1970 in the USA (Rapaport & Eisenreich, 1989, Oliver et.al., 1989). Van Zoest and Van Eck found that in the Scheldt, HCB was present in trace amounts from around 1900, but peak concentrations were quite sharply centred on 1970. Peak concentrations on the Scheldt were approximately half of those found in the Mersey. The unusual pattern of occurrence of HCB in the Mersey can probably be explained by the manufacture of monochlorobenzene which was the first

stage in manufacturing picric acid, an early explosive. This was manufactured in a fairly crude chlorination of benzene in a process which started 'pre-World War I' (Hardie, 1950). It would not be unexpected for hexachlorobenzene to have been produced as by-product during such a reaction. Large quantities of picric acid were made in the Runcorn Widnes region.

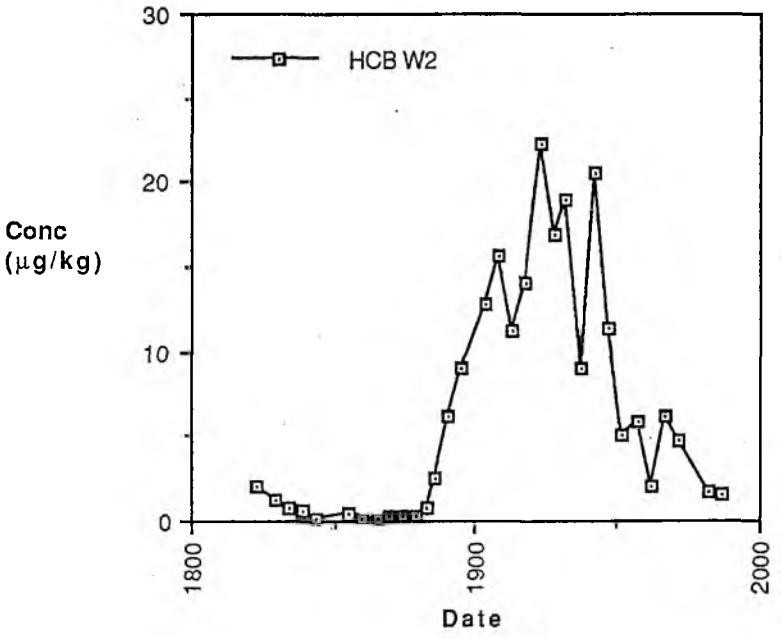

Figure 9-10 Profile of Hexachlorobenzene in Widnes Warth, Core W2

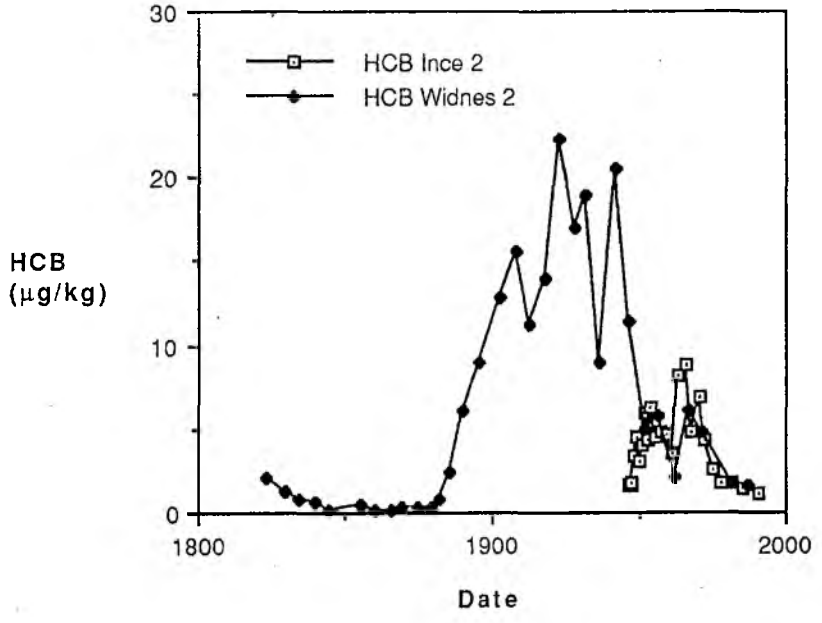

Figure 9-11 Comparison of Profiles of Hexachlorobenzene in Widnes Warth & Ince Marshes

9.1.6 Contamination of the Mersey Estuary by HCH group compounds

There are 8 isomers of hexachlorocyclohexane (HCH), formed by different spatial arrangements of the six chlorine atoms on the ring structure. Commercially prepared HCH contains a mixture of six of these isomers. The gamma - isomer of HCH (the 99% pure form of which is commonly known as Lindane) is the only one of eight isomers to have appreciable insecticidal qualities. The original technical material from which Lindane is prepared contains only about 13% of the gamma form, some 68% of the two alpha stereoisomers and small quantities only of the beta and delta isomers. The biological activity of the different isomers varies widely. Although Lindane is the most common isomer used in Europe and North America, the technical mixture has been widely used elsewhere because of its cheapness. Three isomers were quantified in the present study (α-, β- & γ-). It is known that the analytical methods used in this study were adequate to exclude any interference by Methyl Hexachlorocyclohexane with quantitation of HCH which has been a problem in the past (see McNeish et.al., 1994)

β-HCH is the most prominent member of the HCH group as an environmental residue in the study area. The concentration of β-HCH starts to increase slowly from around 1900 until 1940 when there was a rapid increase (see Figure 9-12). There was a very clear peak in concentration (>150 $\mu g\ kg^{-1}$) of β-HCH in the late 1940s followed by a rapid decline to 1960 with concentrations then declining more slowly to low levels at the surface.

The pattern of contamination by α-HCH is very similar to that of β-HCH although concentrations are much lower. The pattern of γ-HCH is similar although concentrations are hardly above the limit of detection. In the absence of the other isomers, the pattern would not be significant but the presence of all three isomers suggests that the estuary was originally contaminated by technical mixtures of the isomers but that the α-HCH and particularly the γ-HCH were more labile than β-HCH.

This overall pattern is consistent with what is known about the manufacturing and use of this group of compounds. The main production of Lindane is thought to have started around the time of World War II with ICI at Runcorn holding the patent and being a major manufacturer.

It is not clear from the information currently available as to whether the early increase in concentration of α-HCH represents environmental contamination at the time that the sediments were laid down or slow diffusion down the core profile from the more contaminated layers above. The HCH compounds may be more susceptible to this latter process than the much more hydrophobic DDT or PCB group compounds.

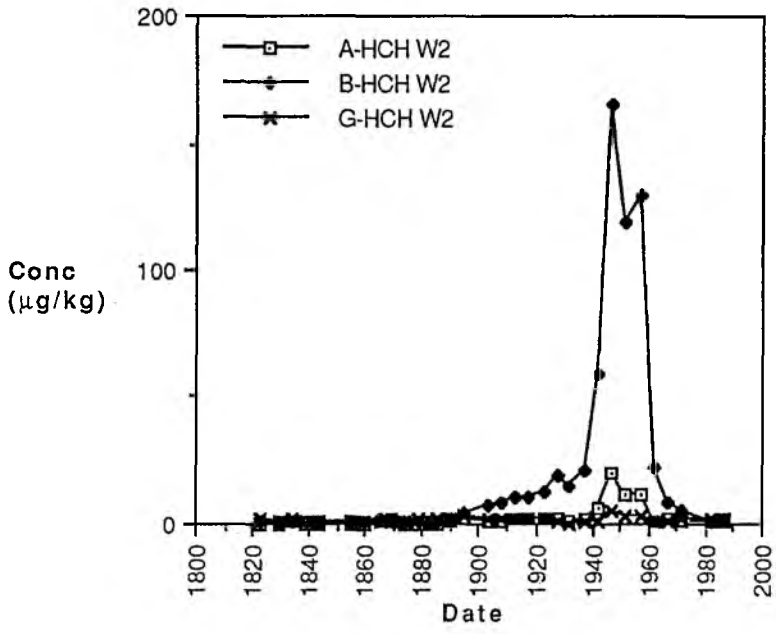

Figure 9-12 Profile of HCH group compounds, Widnes Warth, Core W2

It is worth noting that the pattern of variation in concentrations of the HCH compounds is very consistent between replicate cores (eg see Figure 9-13), even for compounds such as α-HCH which are only present at low concentrations. This implies that the existence of a large differential in concentration of β-HCH during the 1940s & 1950s between Widnes Warth cores and the Ince Marsh cores (see Figure 9-14) is significant in terms of the behaviour and movement of the substance. The existence of the differential suggests that there must have been a large concentration gradient between Widnes and Ince during the 1940s and 1950s but that this declined until the 1970s when both sites had reached the same low levels. This would happen if the sediment contamination continued to disperse after input had ceased. Once the upstream site had reached a similar concentration to the downstream site, net input to the latter could no longer occur and concentrations at both sites would decline as dispersal and breakdown continued.

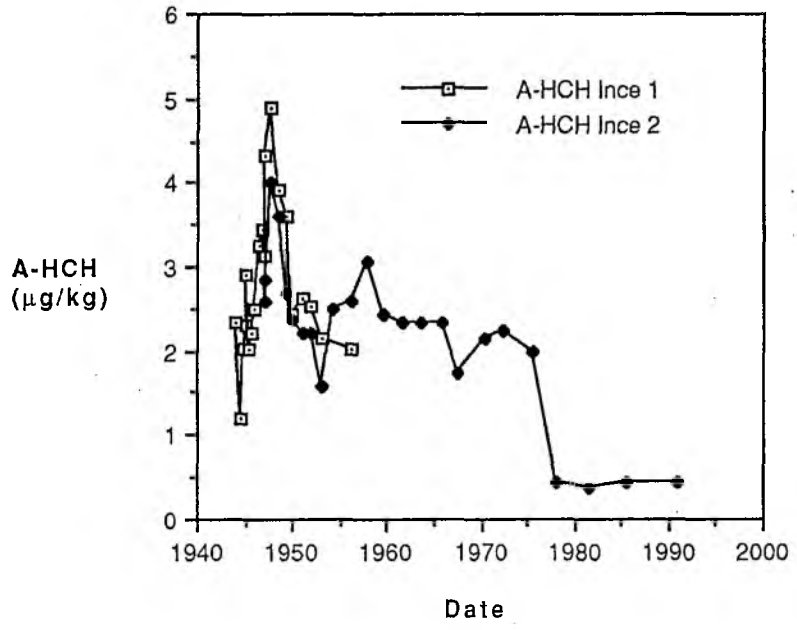

Figure 9-13 Profile of α-HCH, Ince Marsh, Cores I1& I2

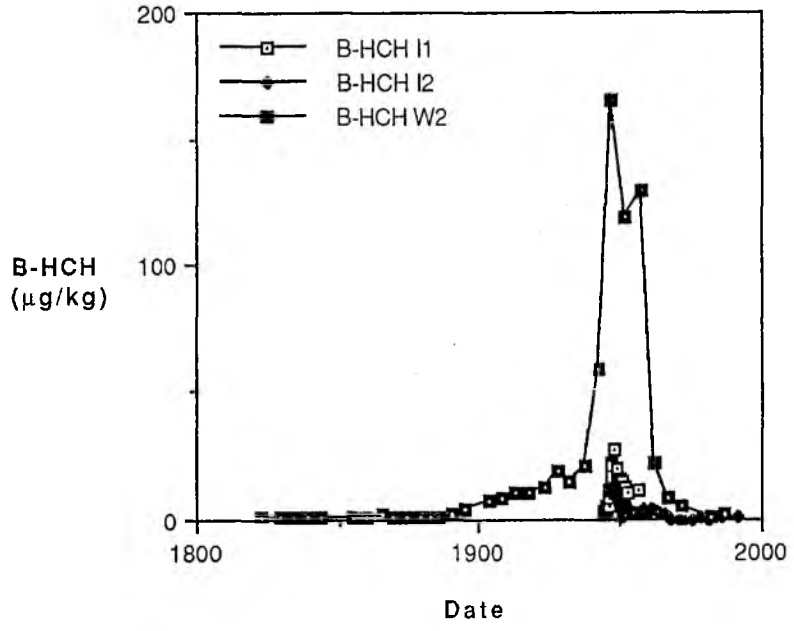

Figure 9-14 Comparison of β-HCH profiles at Ince and Widnes Warth marshes

9.1.7 Contamination of the Mersey Estuary by other Organochlorines

It is very difficult to positively identify all of the chemicals which are contained in very contaminated samples such as those from the Mersey without inordinate amounts of time and money. The main difficulties are because the absolute concentrations of the materials of interest are quite low, making it difficult/impossible to detect them using mass spectrometric detection (GCMS), exacerbated by the large overall number of halogenated compounds in the sample which makes it very difficult to use twin column verification using the more sensitive Electron Capture Detector. However, there are a large number of other chemicals present, some of which on a single column gas chromatograph are 'identified' as pesticides. Although it is considered that these identifications are unlikely to be correct, the results for three compounds which identify as Heptachlor, Endrin and Aldrin are presented in Figure 9-15 - Figure 9-17 because of their very clear patterns in concentration through time.

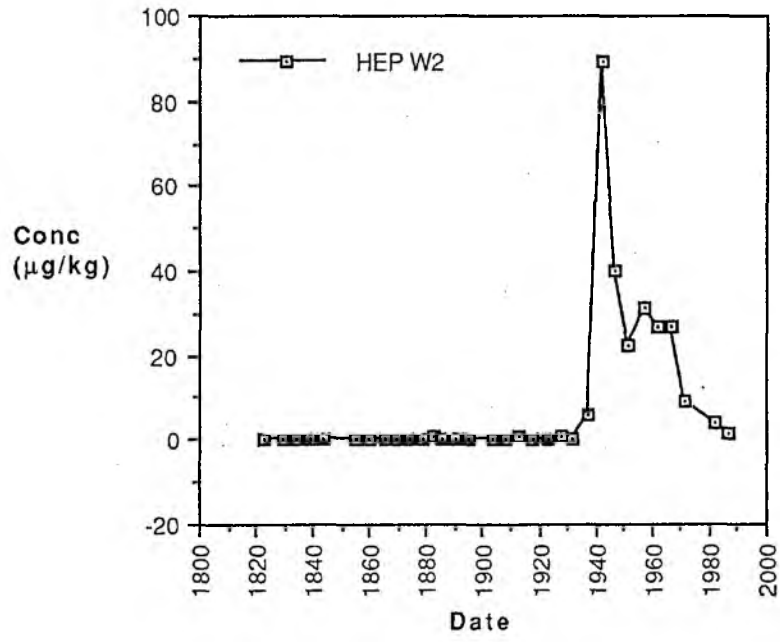

Figure 9-15 Profile of 'Heptachlor' in Widnes Warth Core W2

The substance identified as 'Heptachor' is notable by its rapid appearance in early 1940, subsequently continually declining to very low levels at the surface.

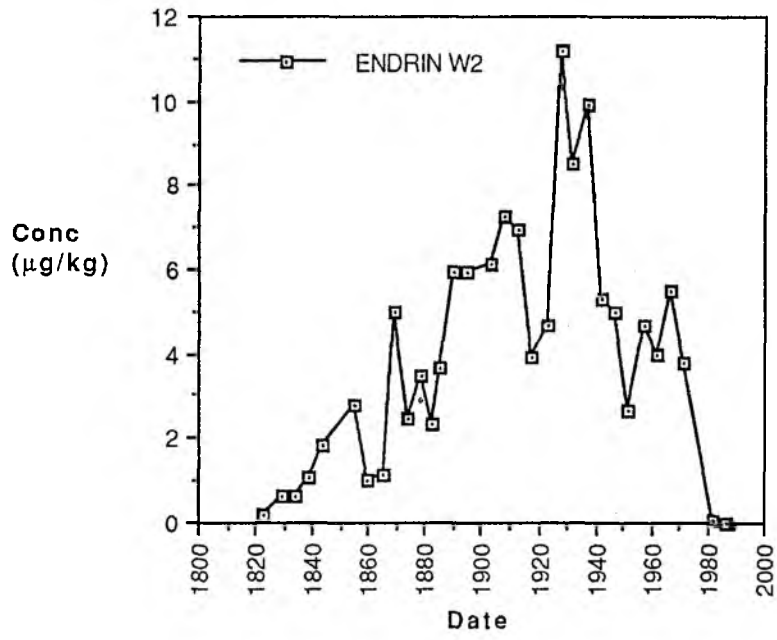

Figure 9-16 Profile of 'Endrin' in Widnes Warth Core W2

Authentic Endrin is an organochlorine, cyclodiene insecticide once widely used although most uses have now been stopped. It is a persistent compound which is poorly degraded and has the potential for bioaccumulation.

The 'Endrin' detected in this study was, with Hexachlorobenzene, the only other possibly halogenated material studied to date which started to increase in concentration before 1900. In the case of 'Endrin', the increase starts right at the bottom of the core around 1920. This pattern of occurrence makes it extremely likely that this substance is NOT correctly identified.

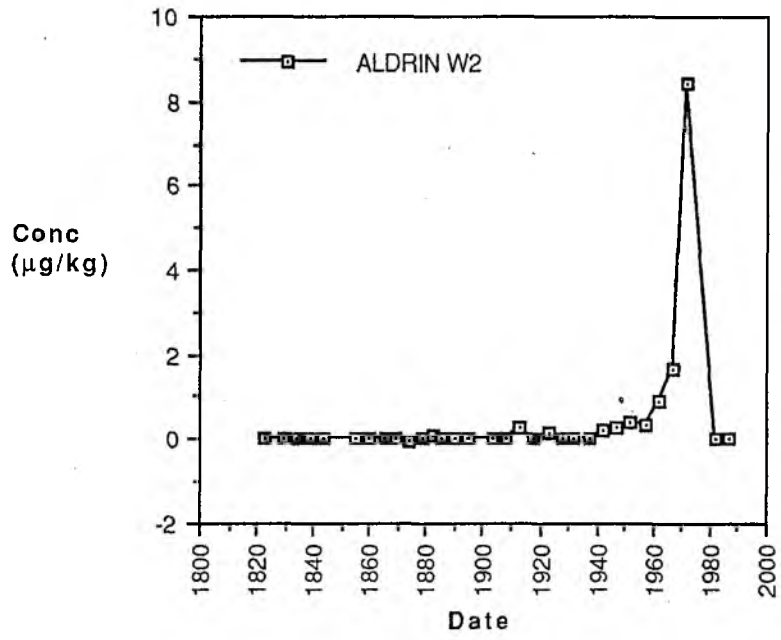

Figure 9-17 Profile of 'Aldrin' in Widnes Warth Core W2

The 'Aldrin' detected in this study only really started to increase after 1950 to a peak in concentration around 1970 followed by a rapid decline to non-detectable.

Authentic aldrin and dieldrin are stereochemically related, aldrin being rapidly metabolised to a form of dieldrin. All approvals for products containing dieldrin in the UK ceased in March, 1989 although the few remaining uses of aldrin in agriculture were allowed to continue until the end of 1992.

10. The revealed history of contamination by Organochlorines in the Ribble Estuary

The Ribble estuary is not as contaminated with organochlorines as the Mersey Estuary although the patterns through time are very similar. The most striking pattern in the Ribble cores is that revealed by the very abrupt increase in concentration (to nearly 100 µg kg^{-1}) of ΣDDT (Figure 10-1) which is very similar (although at a much lower concentration) to that seen in the Mersey. The abrupt increase was followed by a much slower decline to the surface.

The isomer composition of the DDT residues changes with time within the cores (Figure 10-2) but it is notable that a peak in concentration of pp-DDT is apparent at the time DDT first appears in the sediments. As in the Mersey, it is also notable that pp-DDD (the anaerobic breakdown product) forms a very significant component of the DDT residues and pp-DDE only a small proportion.

The replicate cores from Banks Marsh on the Ribble are basically similar to each other in DDT concentration although the fluctuations in concentration between 1955 and 1965 in core BM1 (which was not analysed earlier than 1950 due to cost constraints) are very wide for reasons which are not readily apparent.

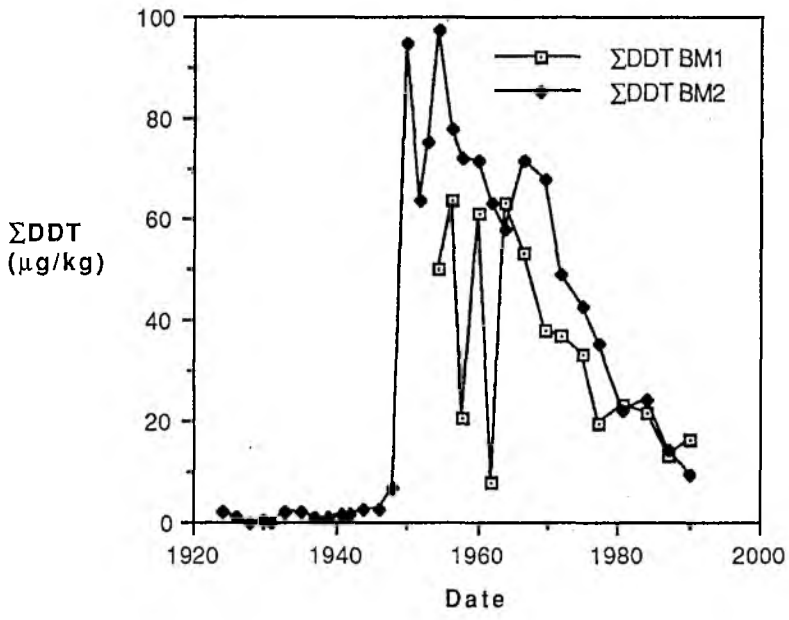

Figure 10-1 Contamination of the Ribble estuary by DDT

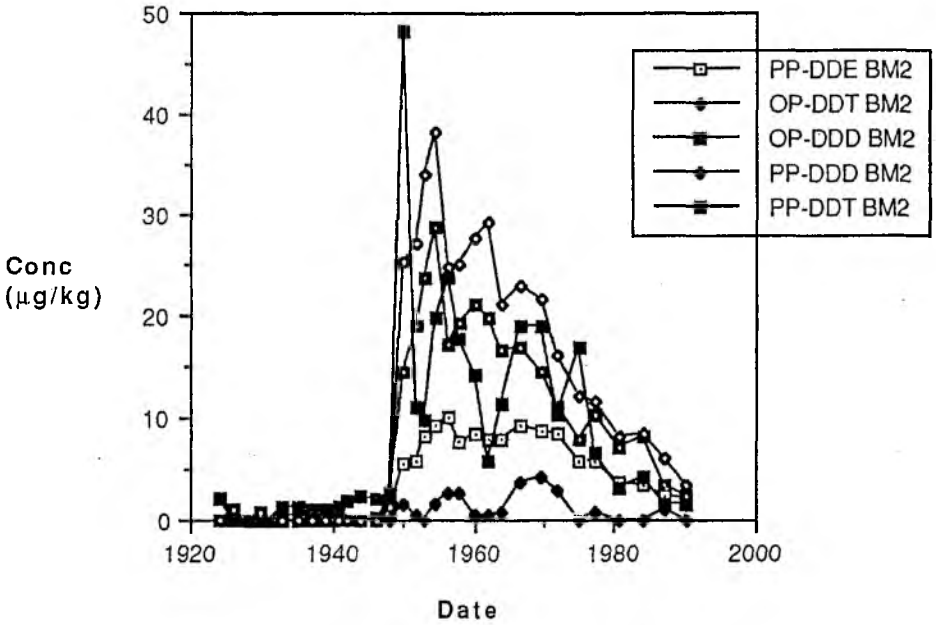

Figure 10-2 Contamination of the Ribble estuary by various DDT group compounds

Such differences in concentration between the replicate cores are not apparent for the PCBs (see Figure 10-3 & Figure 10-4) expressed either as ICES congeners or as Arochlors. It is concluded from this evidence and the similarity of metals concentrations that the two cores, BM1 & BM2 are good replicates of each other and that the differences in concentration seen for ΣDDT are idiosyncratic and do not reflect a general difference between the cores.

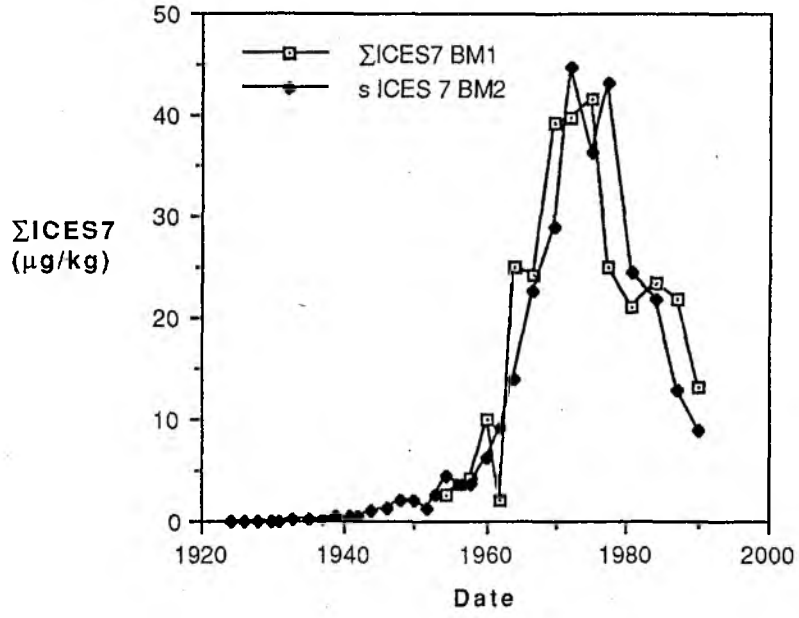

Figure 10-3 Contamination of the Ribble estuary by PCBs (as ΣICES7)

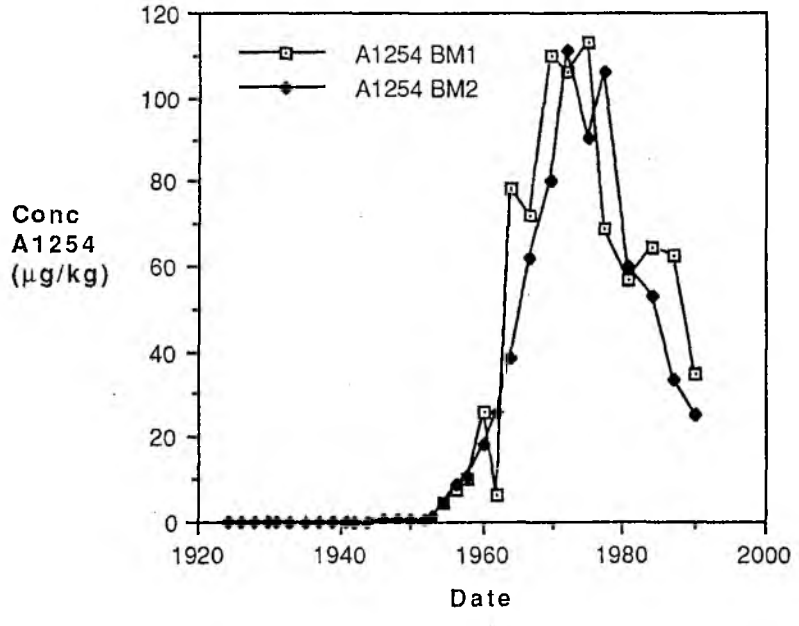

Figure 10-4 Contamination of the Ribble estuary by PCBs (as A1254)

Most of the other organochlorines included in the analytical method were not present at significant concentrations in the Ribble cores (although it should be noted that no separate analyses were conducted for Dieldrin for reasons associated with cost). However, one organochlorine with an interesting pattern which deserves mention is Hexachlorobenzene (see Figure 10-5). Unlike in the Mersey, this does not appear in the sediments until the late 1940s when there was a sharp increase to 13 $\mu g\ kg^{-1}$ followed by an equally rapid decline. Then, (in both cores, since data are available for both BM1 & BM2), concentrations rose to a subsidiary peak around 1970, followed by steady decline to the surface. Concentrations and timing are similar to those observed in the Scheldt (Van Zoest & Van Eck, 1993).

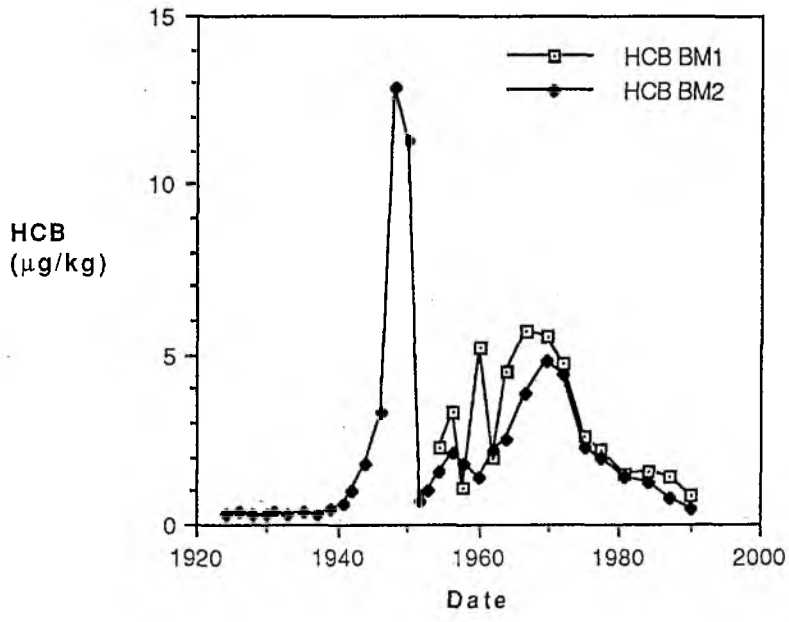

Figure 10-5 Contamination of the Ribble estuary by Hexachlorobenzene

11. Comparison of sediment contamination in the Mersey and Ribble Estuaries

The estuary of the Ribble is some 60 km to the north of the Mersey, the direction in which residual currents and thus net sediment transport occurs. Fine contaminated sediment moving out of the Mersey region, thus might accumulate within the Ribble and there is evidence within the cores that this influence might be quite significant.

There are no *a priori* reasons to expect the background levels of mercury in either the Mersey or the Ribble catchments to differ. The major source of mercury within the region has been the chemical industry in the Runcorn / Widnes area (with some smaller contributions from elsewhere in the Mersey estuary). There has been a significant increase in mercury concentrations over background in the Ribble but peak concentrations of nearly 3.0 mg kg^{-1} were not reached until the 1970s. If the artifact due to sand at the bottom of the Banks Marsh cores is ignored (as explained in Section 8) it can be seen (Figure 11-1) that there was probably only a very slow increase in mercury concentrations above background during the late 19th and early 20th centuries. The rate of increase accelerated towards the 1970s. Mercury concentrations in the Ribble first

stabilised as Mersey concentrations started to decline in the late 1970s and then started to decline more rapidly as Mersey concentrations approached those in the Ribble.

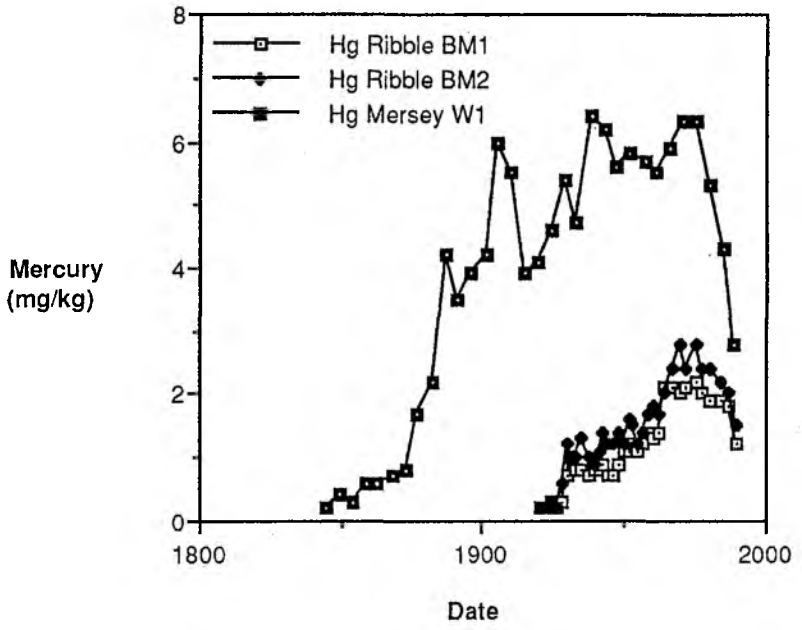

Figure 11-1 Comparison of contamination by Mercury in the Mersey and the Ribble Estuaries

Copper concentrations in the Mersey (Figure 11-2) were very much higher than in the Ribble, reaching a peak concentration of >600 mg kg^{-1} by World War I. Although there were subsequent fluctuations, concentrations declined very rapidly after 1960 whereas in the Ribble the slow rate of increase continued until 1970 since when there has only been a slow rate of decrease despite the concentration in the Mersey now being very similar to that in the Ribble.

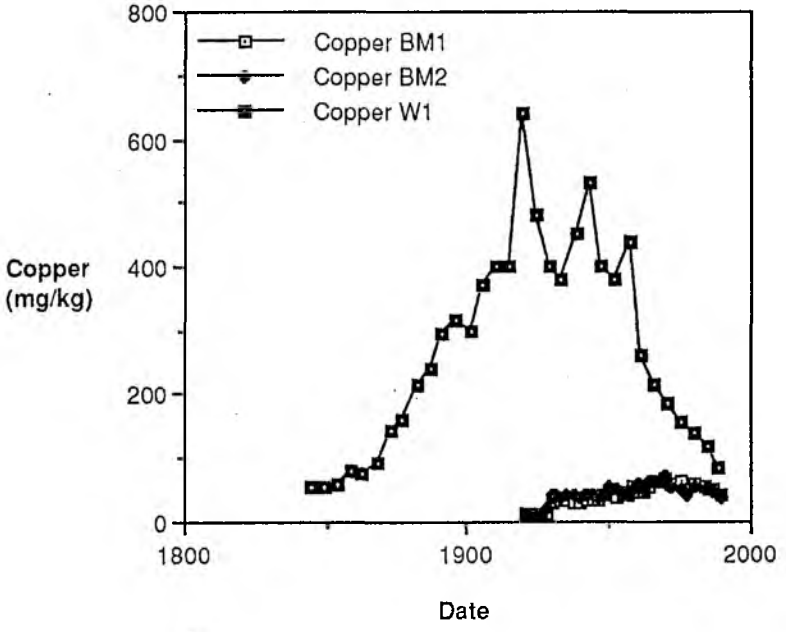

Figure 11-2 Comparison of contamination by Copper in the Mersey and the Ribble Estuaries

A very similar pattern is also evident for chromium (see Figure 11-3) although the discrepancy in timing between the two rivers is even more marked. The peak in concentration of >300 mg kg^{-1} in the Mersey was reached by around 1910 which has been followed by a slow but fairly constant decline to the surface. Throughout this period of decline, the concentrations in the Ribble continued to increase to a peak concentration of just less than 100 mg kg^{-1} with only very small evidence of a decline starting in the last slices of the cores, despite the Mersey concentrations now being only just >100 mg kg^{-1}.

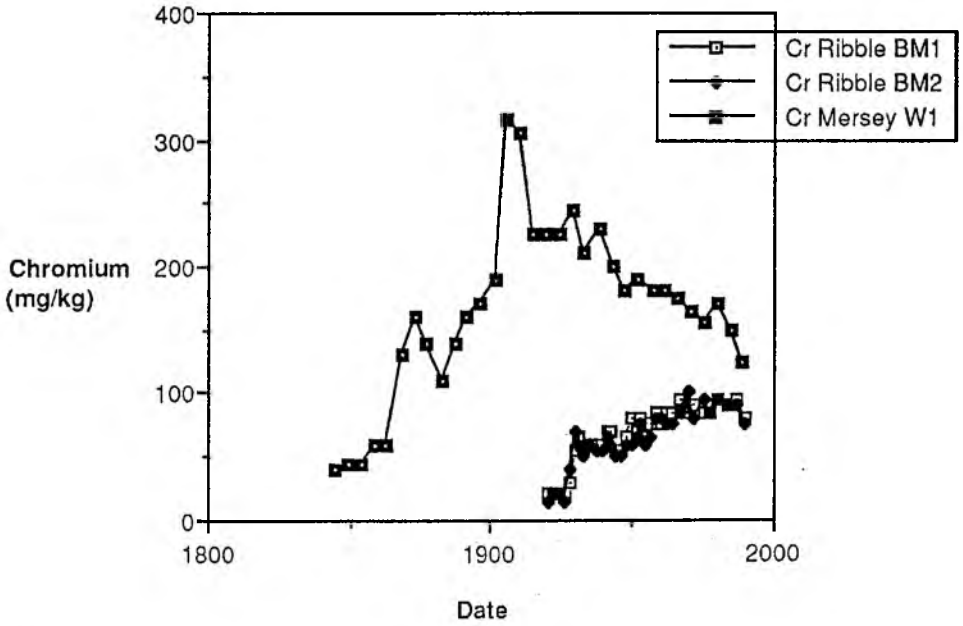

Figure 11-3 Comparison of contamination by Chromium in the Mersey and the Ribble Estuaries

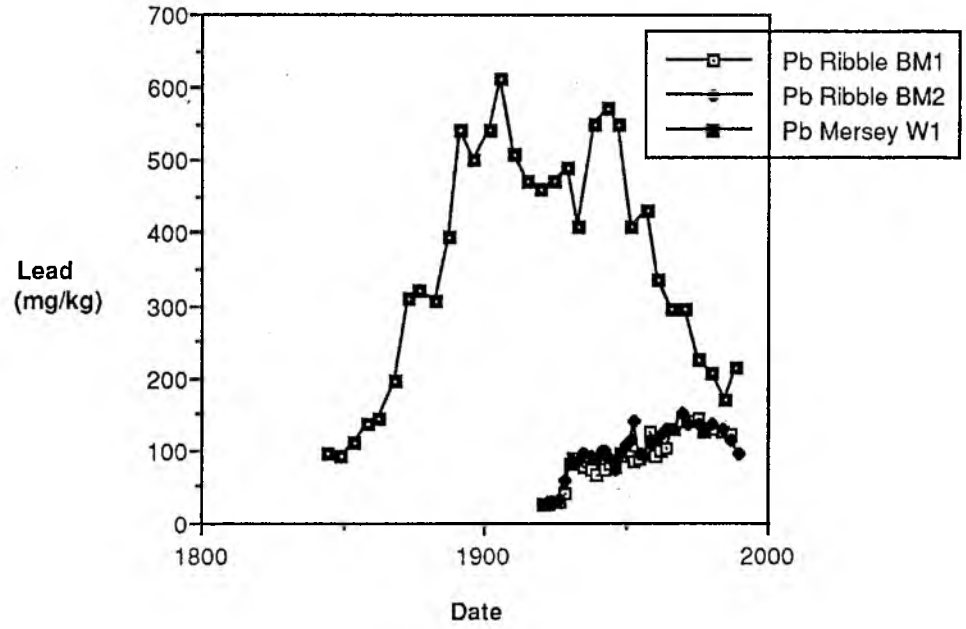

Figure 11-4 Comparison of contamination by Lead in the Mersey and the Ribble Estuaries

Another very similar picture emerges for Lead (Figure 11-4) although the decline in concentration of lead in the Ribble may have been occurring for slightly longer than for chromium.

In contrast to those metals with their industrial origins in the Mersey, the radionuclides have their origins to the north at Sellafield. These exhibit reverse concentration gradients so that concentrations are lower in the Mersey than in the Ribble (eg Figure 11-5 and Figure 11-6)

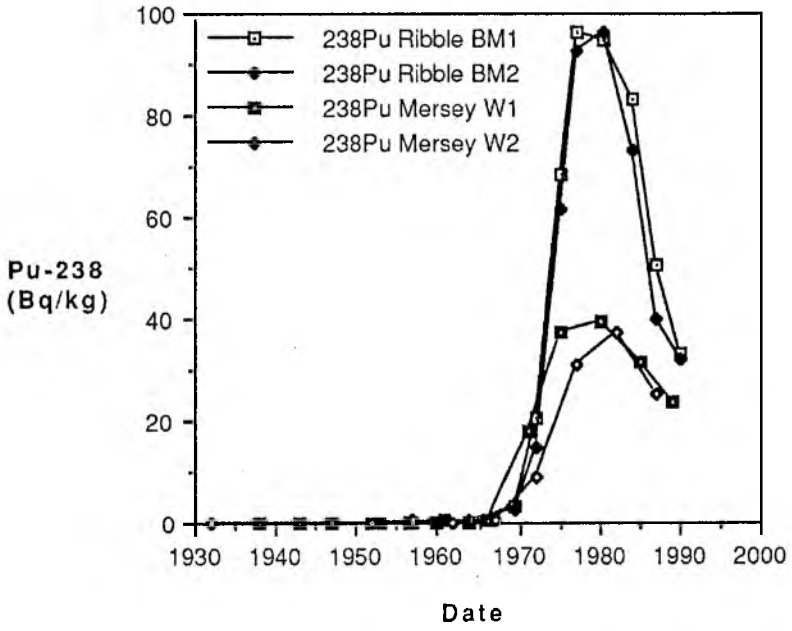

Figure 11-5 Comparison of contamination by 238 Plutonium in the Mersey and the Ribble Estuaries

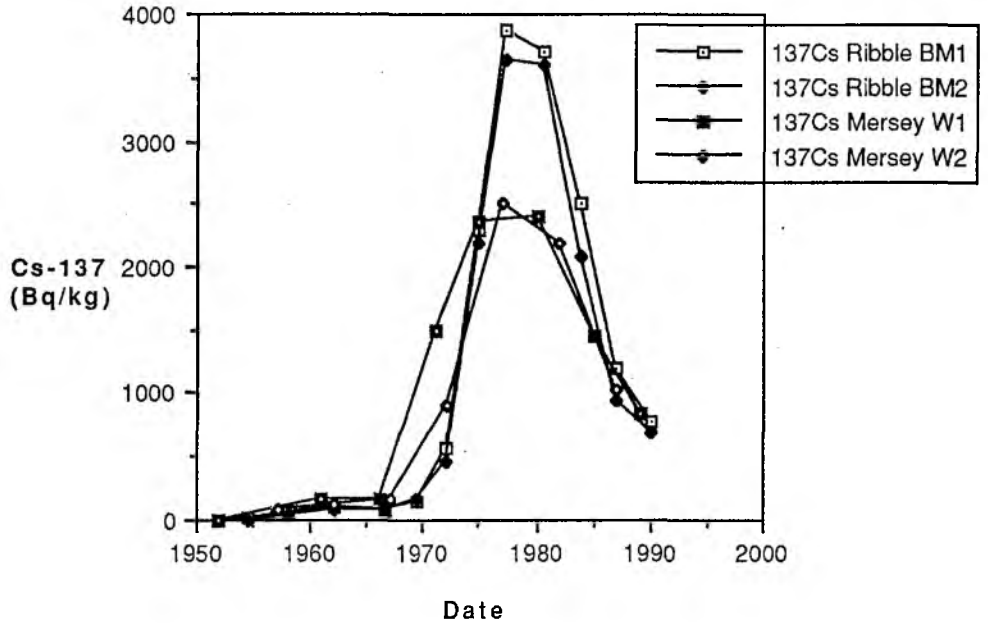

Figure 11-6 Comparison of contamination by 137 Caesium in the Mersey and the Ribble Estuaries

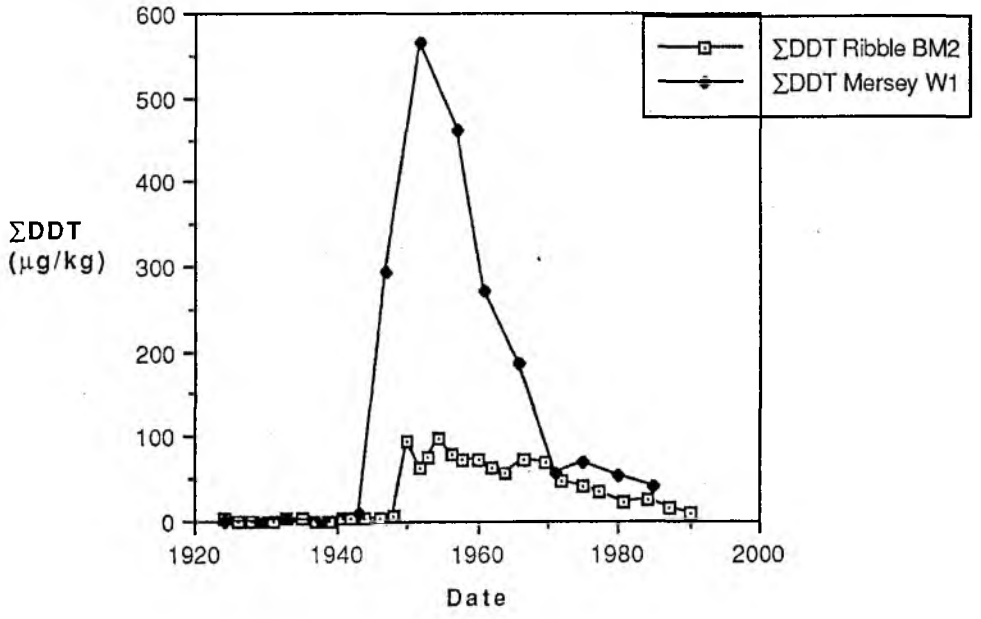

Figure 11-7 Comparison of contamination by ΣDDT in the Mersey and the Ribble Estuaries

The abrupt arrival of DDT in the Mersey core profiles around 1945 is clearly reflected in the Ribble (Figure 11-7) although the difference in shape of the two profiles is very different. If the dating assumptions are sustainable, the DDT pollution of the Mersey had reached the Ribble within five years. The subsequent decline in concentration in the

Ribble was very much slower than in the Mersey where the early peak concentration of nearly 600 μg kg^{-1} ΣDDT had declined to <100 μg kg^{-1} by 1970 when levels in the Mersey were essentially the same as those in the Ribble.

The initial rate of increase in concentration in PCB levels in both the Ribble and the Mersey was very much slower than for DDT (Figure 11-8) and once again, the concentrations in the Mersey were much higher (nearly 150 μg kg^{-1} ΣICES7) than in the Ribble (<50 μg kg^{-1} ΣICES7). The peak concentration in the Mersey was reached before 1970 whilst Ribble concentrations remained near their peak concentration through much of the 1970s, only declining when Mersey concentrations had become very similar.

This pattern suggests that PCB contamination started earlier in the Mersey catchment than the Ribble catchment, that the peak concentration was reached earlier and that declining concentrations had started in the Mersey before the Ribble had reached its peak. This would be consistent with the contamination in the Mersey catchment having largely been the result of manufacturing use whilst the contamination in the Ribble was due to dispersal arising from use elsewhere, possibly in the Mersey. This hypothesis is supported by the coincident decrease in concentrations in both estuaries after the concentrations became similar in the mid 1970s.

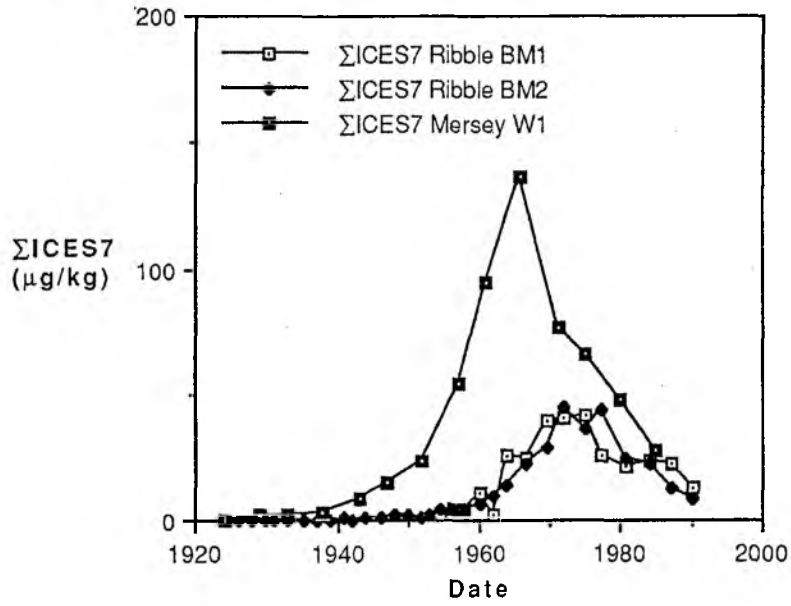

Figure 11-8 Comparison of contamination by PCBs (as ΣICES7) in the Mersey and the Ribble Estuaries

One of the biggest differences in contamination pattern seen between the two estuaries is that for Hexachlorobenzene (Figure 11-9). It was surmised above for the Mersey that the early appearance of Hexachlorobenzene in the sediments might have been associated with the manufacture of Chlorobenzenes for the Picric acid used in early explosives. HCB appears in the Mersey cores in the 1880s, declining to low levels from a peak of >20 μg kg^{-1} by 1950. However, there were no significant concentrations present in the Ribble before the late 1940s when there was a very abrupt increase to >10 μg kg^{-1} followed by an equally rapid decline. Thus whatever event was responsible for this peak is not represented as a feature of the Mersey sediments. However, the increase from the 1950s to a subsidiary peak of c. 5 μg kg^{-1} around 1970 followed by a decline back to low levels was essentially identical in the two estuaries. Such a pattern might be

expected if the initial HCB contamination entering as a by-product of Picric acid production was followed by HCB contamination arising from a separate process. At this moment, there is no direct evidence available.

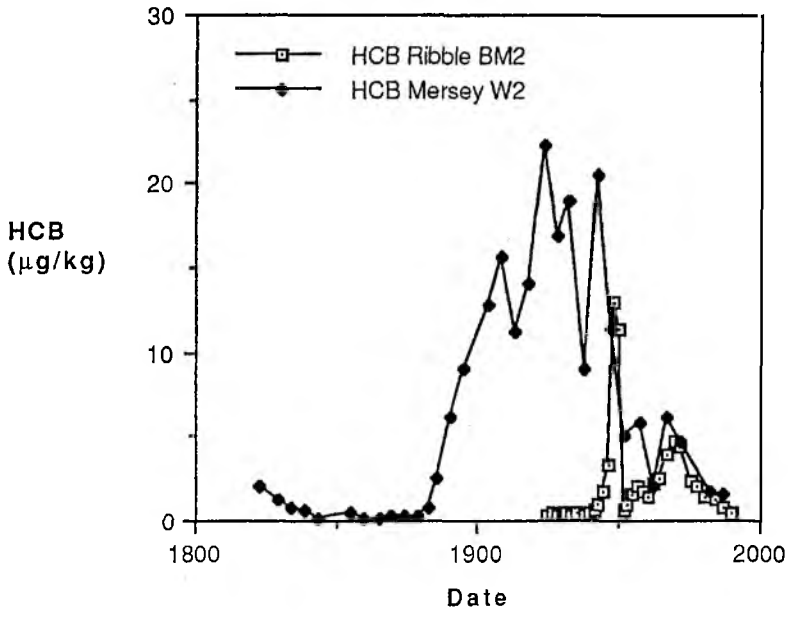

Figure 11-9 Comparison of contamination by Hexachlorobenzene in the Mersey and the Ribble Estuaries

11.1.1 Conclusions

In general, the Ribble estuary is less contaminated with heavy metals and organochlorines than the Mersey estuary.

In contrast, radionuclide levels are higher in the Ribble, reflecting the predominant direction of transport from Sellafield.

The differentials between the estuaries have been maintained throughout the period (since 1920) which is included in the Ribble sediment cores, although contemporary concentrations of many pollutants are now very similar.

A number of 'events' in the pollution history of the Mersey have apparently been reflected in changes in the deposition of contaminants in the Ribble, although there has been a time-lag.

Accumulation of contamination in the Ribble estuary has been continuing until recently, whilst concentrations of contaminants have been decreasing in the Mersey.

In general, the group of observations are consistent with the hypothesis that the main sources of the major contaminants (heavy metals and chlorinated organics) in the Liverpool Bay area have been dispersing from the Mersey region.

A wide range of observations presented here are consistent with the hypothesis that pollutants have dispersed away from areas with high sediment concentrations near to the original source of pollution in a way which means that the contamination on the population of fine particles in the wider area does not reflect all of the decreases in inputs until the source and sink areas are similar in concentration.

12. Summary & General Conclusions

This study has successfully reconstructed the organochlorine contamination history of the Mersey and Ribble Estuaries from sediment cores which had been collected from the estuaries and had been previously studied to determine their radionuclide and stable heavy metal contents (Murdock, 1995).

This new study has re-examined the chronology developed by Murdock and rationalised the observations from two sites on the Mersey and one site on the Ribble estuary, producing linked chronologies for all three sites which are consistent for heavy metals, radionuclides and organochlorines.

There is a clear record in the sediment of the contamination by each heavy metal and organochlorine chemical studied. The record of each material is idiosyncratic and not synchronous although most show an increase in concentration followed be a decrease to the sediment surface.

The record of contamination had originally been connected by Murdock (1995) to a synthetic chronology derived from a mixture of dates obtained from the concentration of various radionuclides in the cores together with historical records of past industrial changes in the uses of contaminating materials. Murdock used mathematical relationships to provide an average chronology for each location although there were some difficulties in reconciling all of the available observations.

Both studies have shown a remarkable level of agreement between concentrations of contaminants in cores taken only a few meters apart. These very close similarities have been used as the main argument for the empirical matching of contamination profiles between adjacent cores, based on stable lead concentrations.

Using the empirical corrections, it has been possible to demonstrate that there have been minor differences in sedimentation rate between the cores at different times. Corrections for these differences, improve the fit between all of the other contaminant profiles in the replicate cores.

The pragmatic approach has been taken that sedimentation patterns at each of the locations studied have been idiosyncratic and have not conformed with simple mathematical relationships so that site specific chronologies have been reconstructed, with intermediate points interpolated between the time signals used for dating.

Fortuitously, the sedimentation rates at Widnes Warth have been virtually constant through time. Extrapolation through the time-signals using linear regression has then been used as the best available method for dating the bottom sections of the cores. No improvement will be possible without utilising another technology to fix a time signal lower down the cores.

The concentrations on fine particles of all of the contaminants studied here have radically declined after inputs have decreased, although the rates have differed at the various locations.

The results show that for the majority of contaminants, a combination of contemporary inputs and the recycling of sedimentary deposits still results in the contamination of fine particles currently accumulating on saltmarsh areas.

The exception to the last statement is Arsenic for which inputs and recycling are now such that fresh particles are virtually no more contaminated than particles deposited in the 1820s.

The results show clearly that there has been a large decline in the contamination of surface sediments by both PCBs and DDT group compounds, although this still leaves the surface sediments contaminated at relatively high levels compared to the wider background. Since new inputs of these materials should now be negligible, this degree of contamination must represent the recycling of buried material.

The results show that there has been very significant contamination of the Mersey system with DDT group compounds which appeared very rapidly in the sediments after manufacture had started in Trafford Park in 1943.

A similar pattern of appearance applies to the HCH group of compounds after the start of their manufacture at Widnes/Runcorn although only the alpha and beta isomers remain in the sediments.

Hexachlorobenzene is the only major chlorinated hydrocarbon positively identified in this study which is present in significant amounts early in this century. The unusual pattern of occurrence of HCB in the Mersey can probably be explained by the manufacture of monochlorobenzene as a precursor for the explosive, Picric Acid.

Comparison of the contamination levels of the sediments collected at Ince Marsh and Widnes Warth shows that during the lower part of the Ince cores (c. 1940-50), there were concentration differentials for many contaminants between the two locations, indicatingthat there were sources in Runcorn/Widnes region.

Later, the changes in concentrations became virtually identical at both sites, suggesting that for such contaminants, concentrations on fine particles within the estuary are now governed mainly by recycling and not contemporary inputs with levels declining as pollutants disperse and degrade.

Dispersal of pollutants from the Mersey region appears to be connected with the accumulation of sedimentary contaminants in the Ribble estuary.

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Index to Data Appendices

GROUP A DATA	GROUP B DATA	GROUP C DATA
Sample Code	Sample Code	Sample Code
Core Slice	A-HCH	Pu-238
Depth	B-HCH	Pu-238
Weight	G-HCH	± 2 Sigma
HCB	H/E	Pu-239+240
CON 28	DIELDRIN	± 2 Sigma
HEP	op-DDD	Arsenic
CON 52	ENDRIN	Chromium
ALDRIN	pp-DDD	Copper
CON 101	op-DDT	Mercury
pp-DDE	pp-DDT	Lead
CON 118	ΣDDT	Zinc
op-DDT	ΣHCH	Original Dating Scheme (Murdock)

Continued overleaf

The History of Contamination in Mersey Sediments

CON 153	Am-241	Time Signals
CON 138	± 2 Sigma	Final Dates by interpolation
CON 180	Cs-137	
Σ ICES 7	Cs-137	
Total Arochlor as A1254	± 2 Sigma	
Total Arochlor as 1:1:1 mixture		

Sample Code	Core Slice (cm)	Depth (cm)	Weight (g)	HCB (µg/kg)	CON 28 (µg/kg)	HEP (µg/kg)	CON 52 (µg/kg)	ALDRIN (µg/kg)	CON 101 (µg/kg)	pp-DDE (µg/kg)	CON 118 (µg/kg)	op-DDT (µg/kg)	CON 153 (µg/kg)	CON 138 (µg/kg)	CON 180 (µg/kg)	Σ ICES 7 (µg/kg)	Total Arochlor (µg/kg as 1254)
S31021A	0-3	1.5	94.5	0.9	2.1	1.2	1.1	0.0	1.6	1.3	2.2	0.0	2.3	2.5	1.4	13.1	35.0
S31021B	3-6	4.5	117.9	1.4	2.8	0.9	1.5	1.1	3.2	1.6	3.7	0.0	3.9	4.6	2.2	21.8	62.4
S31021C	6-9	7.5	107.1	1.6	3.0	3.1	1.8	1.2	3.1	1.7	3.6	0.0	4.0	5.2	2.5	23.3	64.2
S31021D	9-12	10.5	137.2	1.5	2.8	2.1	1.6	0.9	2.6	1.6	3.2	0.0	3.7	4.4	2.6	21.0	56.7
S31021E	12-15	13.5	124.0	2.2	3.3	1.4	2.0	1.4	3.5	2.0	3.9	0.0	4.4	5.3	2.7	25.0	69.1
S31021F	15-18	16.5	124.1	2.6	5.3	1.8	3.3	4.1	6.4	3.7	6.2	0.0	7.5	8.5	4.5	41.6	113.0
S31021G	18-21	19.5	130.7	4.7	4.3	1.8	3.4	1.7	6.3	3.3	5.3	0.0	7.1	8.3	5.0	39.7	105.9
S31021H	21-24	22.5	141.7	5.5	3.8	2.3	3.0	1.7	7.4	4.8	5.8	0.0	6.8	8.6	3.9	39.3	110.2
S31021I	24-27	25.5	132.2	5.7	1.2	3.0	1.5	0.9	3.6	3.3	3.9	0.0	4.7	6.0	3.1	24.1	71.9
S31021J	27-30	28.5	144.3	4.5	0.6	2.9	1.1	1.0	4.2	4.8	4.1	0.0	5.0	6.6	3.2	24.9	78.5
S31021K	30-33	31.5	141.3	2.0	0.0	0.6	0.2	0.0	0.5	0.6	0.5	0.0	0.3	0.6	0.2	2.2	6.5
S31021L	33-36	34.5	135.5	5.2	0.6	3.2	0.7	0.8	1.7	7.0	1.4	1.7	1.6	3.0	1.2	10.1	25.8
S31021M	36-39	37.5	132.8	1.1	0.2	1.6	0.2	0.2	0.9	2.4	0.6	0.0	0.7	1.2	0.6	4.3	10.2
S31021N	39-42	40.5	135.0	3.3	0.4	3.4	0.4	0.0	0.8	6.2	0.5	0.5	0.6	0.5	0.6	3.8	7.8
S31021O	42-45	43.5	126.0	2.3	0.5	3.1	0.3	0.3	0.6	6.0	0.3	0.7	0.4	0.0	0.4	2.5	4.2
S31021P	45-48	46.5	128.6														
S31021Q	48-51	49.5	136.0														
S31021R	51-54	52.5	134.2														
S31021S	54-57	55.5	146.3														
S31021T	57-60	58.5	160.5														
S31021U	60-63	61.5	147.0														
S31021V	63-66	64.5	140.4														
S31021W	66-69	67.5	135.9														
S31021X	69-72	70.5	152.9														
S31021Y	72-75	73.5	130.1														
S31021Z	75-78	76.5	135.3														
S31021A1	78-81	79.5	139.4														
S31021B1	81-84	82.5	125.3														
S31021C1	84-87	85.5	140.1														
S31021D1	87-90	88.5	189.5														
S31021E1	90-93	91.5	135.2														
S31021F1	93-96	94.5	168.9														
S31021G1	96-99	97.5	162.4														
S31021H1	99-102	100.5	162.6														

Sample Code	Total Arochlor (µg/kg as 1:1:1)	A-HCH (µg/kg)	B-HCH (µg/kg)	G-HCH (µg/kg)	H/E µg/kg	DIELDRIN (µg/kg)	op-DDD (µg/kg)	ENDRIN (µg/kg)	pp-DDD (µg/kg)	op-DDT (µg/kg)	pp-DDT (µg/kg)	ΣDDT µg/kg	ΣHCH (µg/kg)	Am-241 Bq/kg	± 2 Sigma Bq/kg	Cs-137 Bq/kg	Decay corrected Cs-137 Bq/kg	± 2 Sigma Bq/kg
S31021A	39.6	0.3	0.0	2.4		2.5	4.3		5.0	1.6	4.0	16.2	2.7	292.2	25.6	782.6	838.8	54.6
S31021B	74.2	0.1	0.0	1.9		0.3	3.2		4.4	0.0	4.2	13.4	2.0	395.6	20.9	1200.7	1411.4	60.5
S31021C	81.9	0.2	0.0	3.0		6.7	5.9		7.2	2.3	4.7	21.7	3.2	628.1	22.5	2505.8	3157.0	105.7
S31021D	75.5	0.5	0.0	3.2		7.5	8.0		8.6	2.2	2.9	23.4	3.6	685.1	28.5	3703.4	5117.4	157.0
S31021E	88.4	0.2	0.0	2.3		7.1	4.7		7.1	0.0	5.5	19.3	2.4	823.8	29.7	3870.3	5731.8	159.8
S31021F	146.5	0.1	0.8	2.4		7.0	7.7		14.1	2.2	5.6	33.3	3.3	723.8	30.6	2295.4	3728.5	103.5
S31021G	139.5	0.4	0.0	3.2		6.8	8.5		11.2	1.5	12.3	36.9	3.6	221.6	6.9	559.7	974.4	23.4
S31021H	137.6	0.2	0.0	1.4		13.3	10.8		15.1	1.2	6.2	38.0	1.6	49.7	3.9	148.8	284.1	8.4
S31021I	80.9	0.4	0.0	3.5		0.3	16.9		18.5	2.8	11.8	53.4	3.9	13.2	2.9	91.4	191.4	5.3
S31021J	77.0	0.2	0.7	2.3		7.6	19.1		26.3	3.7	9.6	63.4	3.2	3.7	0.3			
S31021K	8.4	0.0	0.3	0.4	0.0		2.5		2.5	0.0	2.3	7.9	0.7	3.2	1.7	97.2	239.3	3.2
S31021L	43.7	0.1	0.0	0.6	0.5		11.9		16.4	1.3	23.1	61.3	0.7	1.6	0.2			
S31021M	17.5	0.0	0.0	0.2	0.0		7.6		7.7	0.0	2.6	20.4	0.2	1.7	1.5	53.6	155.1	2.3
S31021N	18.9	0.2	0.0	1.0	0.0		14.0		17.6	1.9	23.5	63.7	1.2	0.7	0.1			
S31021O	13.7	0.2	0.0	0.9	0.0		9.8		14.2	1.6	17.8	50.1	1.1	**1.6**		12.0	40.8	2.1
S31021P														0.6	0.1			
S31021Q														**1.4**		**1.1**		
S31021R																		
S31021S																		
S31021T																		
S31021U																		
S31021V																		
S31021W																		
S31021X																		
S31021Y																		
S31021Z																		
S31021A1																		
S31021B1																		
S31021C1																		
S31021D1																		
S31021E1																		
S31021F1																		
S31021G1																		
S31021H1																		

Sample Code	Pu-238 Bq/kg	Decay corrected Pu-238 Bq/kg	± 2 Sigma Bq/kg	Pu-239+240 Bq/kg	± 2 Sigma Bq/kg	Arsenic (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Original Dating Scheme (Murdock)	Time Signals	Final Dates by interpolation
S31021A	32.5	33.3	1.3	165.0	2.8	20.0	80.0	40.0	1.2		270.0	1988.8	1990.0	1990.0
S31021B	47.8	50.6	1.5	236.3	3.4	20.0	95.0	52.0	1.8	120.0	310.0	1985.3		1987.0
S31021C	76.7	83.0	1.9	373.2	4.3	20.0	90.0	54.0	1.9	125.0	320.0	1981.7		1984.0
S31021D	84.7	94.6	2.1	430.5	4.7	20.0	95.0	58.0	1.9	130.0	360.0	1978.2		1980.5
S31021E	84.4	96.5	2.1	442.9	4.8	20.0	85.0	52.0	2.0	125.0	350.0	1974.6		1977.3
S31021F	58.1	68.6	1.6	345.9	4.0	20.0	85.0	62.0	2.2	145.0	440.0	1971.1	1975.0	1975.0
S31021G	17.1	20.7	0.9	194.2	3.1	25.0	90.0	58.0	2.1	140.0	420.0	1967.5		1972.0
S31021H	2.4	3.0	0.3	61.6	1.7	25.0	85.0	66.0	2.0	140.0	420.0	1964.0	1970.0	1969.5
S31021I						25.0	95.0	64.0	2.1	130.0	420.0	1960.4		1966.5
S31021J	0.1	0.2	0.0	16.7	0.4	20.0	85.0	56.0	2.1	102.0	370.0	1956.9		1964.0
S31021K						15.0	85.0	48.0	1.4	100.0	360.0	1953.3		1962.0
S31021L	0.0	0.1	0.0	12.5	0.4	20.0	75.0	46.0	1.3	92.0	320.0	1949.8		1960.0
S31021M						25.0	85.0	56.0	1.4	125.0	370.0	1946.2		1958.0
S31021N	0.1	0.1	0.0	5.1	0.2	15.0	75.0	44.0	1.2	94.0	290.0	1942.6		1956.5
S31021O						20.0	65.0	40.0	1.1	88.0	280.0	1939.1		1954.5
S31021P	0.1	0.1	0.0	0.3	0.1	10.0	80.0	36.0	1.2	84.0	240.0	1935.5	1952.0	1953.0
S31021Q						20.0	70.0	46.0	1.1	92.0	300.0	1932.0		1952.0
S31021R						15.0	80.0	46.0	1.1	92.0	290.0	1928.4		1950.0
S31021S						20.0	65.0	44.0	0.9	96.0	270.0	1924.9	1948.0	1948.0
S31021T						15.0	55.0	34.0	0.7	76.0	210.0	1921.3		1946.0
S31021U						15.0	55.0	34.0	0.7	80.0	220.0	1917.8		1944.0
S31021V						15.0	70.0	32.0	0.9	72.0	200.0	1914.2		1942.0
S31021W						25.0	70.0	36.0	0.8	90.0	210.0	1910.7		1941.0
S31021X						10.0	60.0	28.0	0.8	66.0	160.0	1907.1		1939.0
S31021Y						15.0	60.0	28.0	0.7	72.0	170.0	1903.6		1937.0
S31021Z						10.0	60.0	32.0	0.8	78.0	190.0	1900.0		1935.0
S31021A1						10.0	55.0	32.0	0.8	80.0	180.0	1896.5		1933.0
S31021B1						10.0	65.0	36.0	1.0	90.0	200.0	1892.9		1931.0
S31021C1						15.0	55.0	30.0	0.7	80.0	190.0	1889.4		1930.0
S31021D1						10.0	30.0	14.0	0.3	40.0	100.0	1885.8		1928.0
S31021E1						10.0	20.0	10.0	0.2	30.0	75.0	1882.3		1926.0
S31021F1						10.0	20.0	14.0	0.3	28.0	75.0	1878.7		1924.0
S31021G1						10.0	20.0	9.0	0.2	24.0	60.0	1875.2		1922.0
S31021H1						10.0	20.0	11.0	0.2	24.0	60.0	1871.6		1920.0

Sample Code	Core Slice (cm)	Depth (cm)	Weight (g)	HCB (µg/kg)	CON 28 (µg/kg)	HEP (µg/kg)	CON 52 (µg/kg)	ALDRIN (µg/kg)	CON 101 (µg/kg)	pp-DDE (µg/kg)	CON 118 (µg/kg)	op-DDT (µg/kg)	CON 153 (µg/kg)	CON 138 (µg/kg)	CON 180 (µg/kg)	Σ ICES 7 (µg/kg)	Total Arochlor (µg/kg as 1254)	Total Arochlor (µg/kg as 1:1:1)
S31022A	0-3	1.5	58.9	0.5	0.4	0.4	0.7	0.0	1.4	2.1	1.8	0.0	1.5	2.1	0.9	8.9	25.4	32.9
S31022B	3-6	4.5	122.7	0.8	1.1	0.6	1.0	0.0	2.1	2.3	2.3	1.0	2.2	2.9	1.3	12.9	33.3	47.5
S31022C	6-9	7.5																
S31022D	9-12	10.5	135.9	1.3	2.3	0.9	1.3	0.1	3.0	3.3	3.4	0.0	4.1	4.9	2.7	21.8	53.2	66.8
S31022E	12-15	13.5	121.2	1.4	2.8	0.9	1.5	0.0	3.6	3.8	3.9	0.0	4.4	5.5	2.9	24.5	59.8	79.0
S31022F	15-18	16.5	114.9	2.0	4.5	1.4	2.6	0.0	6.2	5.7	6.4	0.0	7.7	9.7	5.9	43.1	106.1	136.6
S31022G	18-21	19.5	138.7	2.3	3.1	3.5	3.1	0.1	5.9	5.7	4.9	0.0	6.5	8.3	4.6	36.4	90.5	115.1
S31022H	21-24	22.5	118.3	4.4	3.8	2.7	3.6	0.1	8.5	8.3	6.4	3.0	7.4	10.3	4.8	44.7	111.4	139.4
S31022I	24-27	25.5	148.8	4.8	0.8	4.3	1.6	0.1	4.9	8.8	4.3	2.7	5.6	8.1	3.6	29.0	80.3	81.2
S31022J	27-30	28.5	151.6	3.9	0.6	3.9	1.3	0.1	3.8	9.3	3.5	2.0	4.4	6.1	2.8	22.5	61.9	61.4
S31022K	30-33	31.5	139.2	2.5	0.5	3.1	0.9	0.0	2.5	7.9	2.2	0.9	2.2	4.1	1.5	13.9	38.3	39.6
S31022L	33-36	34.5	119.9	2.2	0.4	2.6	0.5	0.1	1.5	7.8	1.3	0.6	1.4	2.9	1.1	9.1	25.8	25.4
S31022M	36-39	37.5	136.3	1.4	0.2	2.7	0.3	0.1	1.1	8.3	0.9	0.5	0.8	2.2	0.7	6.3	18.5	19.3
S31022N	39-42	40.5	133.7	1.8	0.3	3.7	0.0	0.1	0.8	7.7	0.6	1.0	0.6	0.7	0.7	3.8	10.7	11.1
S31022O	42-45	43.5	126.8	2.1	0.3	4.5	0.0	0.0	0.7	9.9	0.4	1.5	0.7	0.5	1.2	3.8	9.0	0.0
S31022P	45-48	46.5	136.0	1.6	0.0	8.0	0.0	0.0	1.0	9.1	0.3	0.5	0.3	2.6	0.3	4.5	4.4	0.0
S31022Q	48-51	49.5	126.6	1.0	0.0	9.6	0.0	0.0	0.7	8.1	0.2	0.0	0.2	1.4	0.2	2.6	1.5	0.0
S31022R	51-54	52.5	134.2	0.7	0.0	1.8	0.0	0.0	0.3	5.8	0.1	0.6	0.1	0.7	0.1	1.4	0.9	0.0
S31022S	54-57	55.5																
S31022T	57-60	58.5	163.3	11.3	0.0	5.0	0.0	0.0	0.5	5.4	0.2	1.5	0.2	1.2	0.2	2.2	0.6	0.0
S31022U	60-63	61.5	122.7	12.9	0.0	4.5	0.0	0.0	0.4	0.7	0.1	0.0	0.2	1.1	0.3	2.1	0.5	0.0
S31022V	63-66	64.5	137.1	3.3	0.0	2.1	0.0	0.0	0.2	0.2	0.2	0.0	0.2	0.6	0.2	1.4	0.4	0.0
S31022W	66-69	67.5	135.7	1.8	0.1	1.1	0.0	0.0	0.2	0.0	0.1	0.0	0.1	0.3	0.2	1.0	0.2	0.0
S31022X	69-72	70.5	140.9	1.0	0.2	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.4	0.0	0.0
S31022Y	72-75	73.5	131.3	0.6	0.1	1.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.6	0.2	1.8
S31022Z	75-78	76.5	144.1	0.5	0.0	0.8	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.4	0.0	0.9
S31022A1	78-81	79.5	139.1	0.3	0.0	0.7	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.2	0.0	0.0
S31022B1	81-84	82.5	115.0	0.4	0.0	0.9	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.3	0.0	0.9
S31022C1	84-87	85.5	134.2	0.3	0.0	0.5	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	1.1
S31022D1	87-90	88.5	178.5	0.4	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.5
S31022E1	90-93	91.5	163.4	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S31022F1	93-96	94.5	160.1	0.3	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S31022G1	96-99	97.5	160.1	0.4	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S31022H1	99-102	100.5	163.3	0.3	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Banks Core 2

Sample Code	A-HCH (µg/kg)	B-HCH (µg/kg)	G-HCH (µg/kg)	H/E (µg/kg)	DIELDRIN (µg/kg)	op-DDD (µg/kg)	ENDRIN (µg/kg)	pp-DDD (µg/kg)	op-DDT (µg/kg)	pp-DDT (µg/kg)	ΣDDT (µg/kg)	ΣHCH (µg/kg)	Am-241 Bq/kg	± 2 Sigma Bq/kg	Cs-137 Bq/kg	Decay corrected Cs-137 Bq/kg	± 2 Sigma Bq/kg	Pu-238 Bq/kg
S31022A	0.1	0.2	1.3	0.0	0.2	2.3	0.0	3.4	0.0	1.6	9.5	1.6	291.1	22.0	705.2	757.7	47.0	31.4
S31022B	0.3	0.0	1.4	0.4	0.4	3.5	0.0	6.0	0.0	1.6	14.4	1.7	330.3	28.0	945.8	1099.7	56.8	37.9
S31022C													524.9	19.7	2086.6	2625.2	89.1	67.8
S31022D	0.3	0.0	1.1	0.2	0.0	8.1	0.0	8.3	0.0	4.3	24.0	1.3	684.9	22.9	3605.0	4908.1	146.7	86.7
S31022E	0.2	0.3	1.3	0.1	0.0	7.1	0.0	8.2	0.0	3.2	22.3	1.7	789.6	27.2	3645.0	5370.0	151.6	81.2
S31022F	0.3	0.0	1.0	0.3	0.0	10.3	0.0	11.5	0.9	6.7	35.1	1.2	617.3	24.7	2193.9	3497.6	96.8	52.4
S31022G	0.2	0.3	0.8	-0.1	0.0	7.9	0.0	12.0	0.0	16.8	42.4	1.3	163.2	10.2	473.5	816.9	22.9	12.3
S31022H	0.3	0.4	1.1	0.0	0.0	11.1	0.0	16.1	0.0	10.4	48.9	1.9	44.5	3.5	170.9	319.0	8.0	2.2
S31022I	0.2	0.3	0.5	0.1	0.3	14.4	0.0	21.5	1.5	19.0	68.1	1.1	14.8	1.7	87.4	176.6	3.3	
S31022J	0.3	0.4	0.7	-0.1	0.5	16.8	0.0	22.8	1.6	19.0	71.5	1.3	2.9	0.3				0.2
S31022K	0.2	0.4	0.5	-0.1	0.4	16.5	0.0	21.1	0.0	11.3	57.8	1.1	2.4	1.5	87.4	206.7	2.8	
S31022L	0.3	0.4	0.4	0.1	0.0	19.8	0.0	29.1	0.0	5.7	63.1	1.1	1.3	0.2				0.1
S31022M	0.2	0.5	0.4	0.0	0.0	21.0	0.0	27.7	0.0	14.3	71.8	1.1	**1.5**		39.8	110.2	2.2	
S31022N	0.9	0.7	1.3	0.4	0.0	19.1	5.0	25.1	1.6	17.6	72.1	2.9	0.6	0.1				0.1
S31022O	0.9	0.9	1.3	0.5	0.0	17.2	5.9	24.7	1.0	23.7	78.0	3.2	1.6	1.5	8.3	26.9	2.2	
S31022P	1.0	1.2	1.5	0.4	0.0	28.7	3.0	38.1	1.1	19.7	97.2	3.8	0.6	0.1				0.1
S31022Q	0.7	1.0	1.0	0.4	0.0	23.7	3.2	33.9	0.0	9.9	75.5	2.6	**1.5**		**1.1**			
S31022R	0.0	0.5	0.8	0.6	0.0	18.9	4.3	27.1	0.0	11.1	63.6	1.3						
S31022S																		
S31022T	0.0	0.3	1.0	0.4	0.0	14.6	2.8	25.2	0.0	48.2	94.8	1.3						
S31022U	0.0	0.0	1.8	0.0	0.0	2.1	2.6	1.4	0.0	2.7	6.9	1.8						
S31022V	0.0	0.2	1.4	0.4	0.0	0.0	3.2	0.0	0.0	2.2	2.4	1.7						
S31022W	0.0	0.0	1.3	0.0	0.0	0.0	3.9	0.0	0.0	2.5	2.5	1.3						
S31022X	0.0	0.0	1.2	0.5	0.0	0.0	3.9	0.0	0.0	1.7	1.7	1.2						
S31022Y	0.0	0.0	0.8	0.2	0.0	0.5	0.2	0.0	0.0	1.3	1.8	0.8						
S31022Z	0.0	0.0	0.7	0.2	0.0	0.2	0.0	0.0	0.0	1.0	1.2	0.7						
S31022A1	0.0	0.0	1.1	0.2	0.0	0.1	0.4	0.0	0.0	1.1	1.2	1.1						
S31022B1	0.0	0.0	0.9	0.6	0.2	0.7	0.0	0.0	0.0	1.3	2.0	0.9						
S31022C1	0.0	0.0	0.9	0.2	0.2	0.6	0.8	0.0	0.0	1.4	2.1	0.9						
S31022D1	0.0	0.0	1.7	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	1.7						
S31022E1	0.0	0.0	0.6	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.7	0.6						
S31022F1	0.0	0.0	1.7	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.1	1.7						
S31022G1	0.0	0.0	0.6	0.4	0.4	1.1	3.8	0.0	0.0	0.0	1.1	0.6						
S31022H1	0.0	0.0	0.6	0.0	0.0	0.0	2.0	0.0	0.0	2.0	2.1	0.6						

Sample Code	Decay corrected Pu-238 Bq/kg	± 2 Sigma Bq/kg	Pu-239+240 Bq/kg	± 2 Sigma Bq/kg	Plut Ratio	Arsenic (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Original Dating Scheme (Murdock)	Time Signals	Final Dates by interpolation
S31022A	32.2	1.2	160.3	2.9	0.20	20	75	38	1.5	96	230	1988.8	1990.0	1990.0
S31022B	39.9	1.5	193.4	3.3	0.21	20	90	48	2.0	115	280	1985.3		1987.0
S31022C	73.4	2.0	325.9	4.4	0.23	25	90	52	2.2	130	310	1981.7		1984.0
S31022D	96.4	2.2	431.1	4.9	0.22	25	95	54	2.4	135	340	1978.2		1980.5
S31022E	92.7	2.1	423.2	4.7	0.22	20	85	44	2.4	125	290	1974.6		1977.3
S31022F	61.4	1.7	337.8	4.2	0.18	20	95	52	2.8	135	330	1971.1	1975.0	1975.0
S31022G	14.8	0.8	161.0	2.9	0.09	25	80	56	2.4	135	370	1967.5		1972.0
S31022H	2.8	0.4	61.1	1.8	0.05	30	100	70	2.8	150	420	1964.0	1970.0	1969.5
S31022I						30	85	64	2.4	130	420	1960.4		1966.5
S31022J	0.3	0.0	14.4	0.7	0.02	30	75	64	2.0	130	390	1956.9		1964.0
S31022K						25	75	52	1.7	120	340	1953.3		1962.0
S31022L	0.2	0.0	11.2	0.3	0.02	30	80	60	1.8	115	370	1949.8		1960.0
S31022M						20	80	52	1.7	115	320	1946.2		1958.0
S31022N	0.1	0.0	4.2	0.2	0.03	25	65	48	1.4	92	300	1942.6		1956.5
S31022O						20	60	48	1.2	96	300	1939.1		1954.5
S31022P	0.1	0.0	0.2	0.1	0.35	35	75	52	1.5	140	370	1935.5	1952.0	1953.0
S31022Q						25	65	52	1.6	115	320	1932.0		1952.0
S31022R						25	60	56	1.2	105	320	1928.4		1950.0
S31022S						20	60	42	1.4	95	250	1924.9	1948.0	1948.0
S31022T						20	50	36	1.2	75	230	1921.3		1946.0
S31022U						25	50	40	1.2	90	240	1917.8		1944.0
S31022V						20	60	42	1.4	100	230	1914.2		1942.0
S31022W						20	65	44	1.1	100	240	1910.7		1941.0
S31022X						25	55	36	0.9	88	230	1907.1		1939.0
S31022Y						25	55	40	1.0	92	250	1903.6		1937.0
S31022Z						20	60	44	1.3	96	220	1900.0		1935.0
S31022A1						20	50	38	1.0	84	200	1896.5		1933.0
S31022B1						20	60	40	1.0	86	200	1892.9		1931.0
S31022C1						15	70	44	1.2	86	220	1889.4		1930.0
S31022D1						15	40	22	0.6	58	150	1885.8		1928.0
S31022E1						10	15	10	0.2	32	65	1882.3		1926.0
S31022F1						10	20	9	0.3	30	60	1878.7		1924.0
S31022G1						10	20	10	0.2	28	70	1875.2		1922.0
S31022H1						10	15	12	0.2	26	65	1871.6		1920.0

Sample Code	Core Slice (cm)	Depth (cm)	Weight (g)	HCB (µg/kg)	CON 28 (µg/kg)	HEP (µg/kg)	CON 52 (µg/kg)	ALDRIN (µg/kg)	CON 101 (µg/kg)	pp-DDE (µg/kg)	CON 118 (µg/kg)	op-DDT (µg/kg)	CON 153 (µg/kg)	CON 138 (µg/kg)	CON 180 (µg/kg)	ΣICES 7 (µg/kg)	Total Arochlor (µg/kg as 1254)
S31011A	0-3	1.5															
S31011B	3-6	4.5															
S31011C	6-9	7.5															
S31011D	9-12	10.5															
S31011E	12-15	13.5															
S31011F	15-18	16.5															
S31011G	18-21	19.5															
S31011H	21-24	22.5															
S31011I	24-27	25.5															
S31011J	27-30	28.5															
S31011K	30-33	31.5															
S31011L	33-36	34.5															
S31011M	36-39	37.5															
S31011N	39-42	40.5			0.0	13.0	3.2	0.6	9.9	24.1	7.0	4.0	7.2	10.6	4.8	42.7	
S31011O	42-45	43.5															
S31011P	45-48	46.5			0.0	13.3	4.7	0.0	5.7	26.3	4.8	3.2	4.5	7.8	3.8	31.3	
S31011Q	48-51	49.5			0.0	13.8	0.8	0.0	4.7	27.3	3.5	1.7	4.4	7.9	3.8	25.0	
S31011R	51-54	52.5			0.0	12.3	1.2	0.4	2.7	27.6	2.0	0.9	2.6	6.1	2.0	16.6	
S31011S	54-57	55.5			0.0	11.8	1.1	0.0	2.0	26.1	2.1	2.2	2.3	5.9	1.8	15.1	
S31011T	57-60	58.5			0.0	14.0	0.9	0.0	1.8	30.8	2.1	1.4	2.0	5.5	1.5	13.7	
S31002U	60-63	61.5			0.0	11.1	0.3	0.3	1.2	36.7	1.8	0.8	1.5	4.4	1.1	10.2	
S31011V	63-66	64.5			0.0	13.4	0.6	0.2	1.3	39.7	1.9	3.0	1.7	4.7	1.2	11.3	
S31011W	66-69	67.5			0.0	12.6	0.5	0.2	0.9	32.8	1.7	2.5	1.6	4.4	1.1	10.3	
S31011X	69-72	70.5			0.0	11.2	0.1	0.0	0.7	25.6	1.3	2.9	1.1	3.4	0.7	7.3	
S31011Y	72-75	73.5			0.0	11.4	0.0	0.0	0.4	34.0	1.3	4.4	0.8	3.5	0.6	6.6	
S31011Z	75-78	76.5			0.0	10.6	0.0	0.0	0.2	17.6	1.1	1.9	0.7	3.9	0.6	6.4	
S31011A1	78-81	79.5			0.0	9.4	0.0	0.0	0.2	12.9	0.8	5.8	0.5	3.8	0.6	5.9	
S31011B1	81-84	82.5			0.0	11.6	0.0	0.0	0.1	21.9	0.7	4.0	0.8	4.9	0.8	7.3	
S31011C1	84-87	85.5			0.0	15.5	0.0	0.0	0.1	12.5	0.4	13.9	0.6	5.1	0.7	6.9	
S31011D1	87-90	88.5			0.0	19.2	0.0	0.0	0.0	7.4	0.6	12.2	0.4	5.6	0.7	7.3	
S31011E1	90-93	91.5			0.0	23.2	0.0	0.0	0.4	4.9	0.6	14.0	0.7	6.2	0.8	8.6	
S31011F1	93-96	94.5			0.0	24.5	0.0	0.0	0.5	4.0	0.6	12.5	0.7	6.2	0.7	8.8	
S31011G1	96-99	97.5			0.0	18.2	0.0	0.0	0.0	3.5	0.3	8.3	0.3	4.5	0.5	5.6	
S31011H1	99-102	100.5			0.0	22.6	0.0	0.0	0.0	3.1	0.3	8.8	0.5	4.3	0.5	5.6	

Total Arochlor (µg/kg as 1:1:1)	A-HCH (µg/kg)	B-HCH (µg/kg)	G-HCH (µg/kg)	H/E (µg/kg)	DIELDRIN (µg/kg)	op-DDD (µg/kg)	ENDRIN (µg/kg)	pp-DDD (µg/kg)	op-DDT (µg/kg)	pp-DDT (µg/kg)	ΣDDT (µg/kg)	ΣHCH (µg/kg)	Am-241 Bq/kg	± 2 Sigma Bq/kg	Cs-137 Bq/kg	Decay corrected Cs-137 Bq/kg
													171.7		769.6	
													326.2		1679.0	
													338.5		2196.6	
													355.5		2492.0	
													363.6		2320.1	
													163.8		856.9	
													12.2		86.9	
													8.7		78.0	
													3.3		53.6	
													3.6		55.4	
													3.5		63.0	
													1.7		50.1	
	2.0	11.5	1.9	1.3		122.4		205.3	6.3	22.6	384.7	15.5				
													2.7		31.7	
	2.2	10.7	0.5	-0.3		142.1		214.3	4.9	15.9	406.6	13.3				
	2.5	12.4	1.9	1.8		192.1		280.5	3.2	15.7	520.6	16.9	1.8		13.5	
	2.6	15.1	0.4	1.8		176.2		265.9	3.9	15.5	490.0	18.2				
	2.4	16.1	0.5	-0.3		161.6		260.7	3.3	8.2	461.9	19.1				
	3.6	19.9	1.0	1.0		208.2		338.0	3.4	16.8	598.6	24.5				
	3.9	16.8	1.3	5.0		220.2		368.1	5.3	25.7	656.7	22.0				
	4.9	27.4	1.1	1.3		275.1		431.2	4.6	19.0	772.5	33.3				
	4.3	21.1	1.0	0.9		263.5		371.2	4.4	23.0	697.5	26.4				
	3.1	22.2	0.6	2.5		195.5		277.6	0.0	18.0	519.5	25.9				
	3.4	16.8	1.5	1.0		197.7		275.9	5.7	38.9	556.6	21.7				
	3.3	20.2	1.5	0.8		176.1		207.1	2.7	22.2	427.8	24.9				
	2.5	11.8	1.6	2.6		175.2		149.4	6.2	16.7	366.2	15.9				
	2.2	8.6	1.3	2.9		152.4		171.0	2.6	27.3	379.2	12.1				
	2.0	5.8	1.1	2.4		82.1		101.6	2.7	11.7	224.5	8.9				
	2.9	5.2	0.8	2.7		36.8		48.6	2.7	4.4	112.1	8.9				
	2.3	4.2	1.3	1.2		8.8		16.1	1.4	1.3	46.5	7.8				
	2.0	4.3	0.8	0.8		3.5		6.1	0.0	0.0	26.1	7.1				
	1.2	3.6	0.9	0.0		3.9		6.0	0.0	1.5	23.3	5.7				
	2.3	3.1	1.4	1.1		0.9		1.5	0.0	0.0	14.3	6.8				

Ince Core 1

±2 Sigma Bq/kg	Pu-238 Bq/kg	Decay corrected Pu-238 Bq/kg	±2 Sigma Bq/kg	Pu-239+240 Bq/kg	±2 Sigma Bq/kg	Arsenic (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Original Dating Scheme (Murdock)	Time Signals	Final Dates by interpolation
	23.2			119.8		70	130	105	3.1	175	460	1988.5	1990	1991.0
	39.2			202.1		50	160	105	4.6	200	460	1984.2		1985.5
	43.3			220.8		50	160	130	5.4	220	440	1980.0		1981.5
	44.1			230.6		60	160	145	5.7	230	600	1975.8		1978.0
	32.0			189.1		40	170	160	7.3	225	620	1971.5	1975	1975.5
	12.2			122.6		60	180	150	7.2	250	700	1967.3		1972.5
	1.9			45.4		90	160	155	5.1	310	800	1963.0	1970	1970.5
	0.7			23.8		60	180	195	5.5	325	780	1958.8		1967.5
	0.6			21.4		50	165	185	5.9	265	780	1954.5		1965.8
	0.3			12.6		60	155	180	5.6	245	720	1950.3		1963.5
	0.2			7.9		70	165	165	5.6	235	720	1946.1		1961.5
	0.4			9.7		50	160	170	5.9	225	740	1941.8		1959.5
						80	155	170	4.9	290	800	1937.6		1958.0
						60	150	155	4.6	255	680	1933.3		1956.3
						80	160	185	5.9	300	760	1929.1		1954.3
						50	165	130	5.6	230	580	1924.8		1953.0
						70	175	180	5.3	290	800	1920.6	1952	1952.0
						70	165	165	5.3	290	740	1916.4		1951.0
						80	170	210	4.6	275	960	1912.1		1950.0
						70	155	200	4.2	255	840	1907.9		1949.3
						80	180	235	5.0	290	940	1903.6		1948.5
						100	195	240	5.6	305	1060	1899.4		1947.8
						100	195	235	5.2	300	1040	1895.2		1947.3
						80	150	200	4.2	260	860	1890.9		1947.0
						80	150	220	4.3	275	840	1886.7		1946.8
						80	135	230	3.9	240	760	1882.4		1946.5
						70	150	215	4.4	265	660	1878.2		1946.0
						60	130	195	4.3	260	620	1873.9		1945.8
						70	135	190	4.2	260	600	1869.7		1945.5
						70	140	195	4.7	275	600	1865.5		1945.3
						70	135	195	4.6	295	600	1861.2	1945	1945.0
						80	155	205	5.7	330	700	1857.0		1944.8
						80	145	165	5.0	285	680	1852.7		1944.5
						70	140	125	4.6	225	580	1848.5		1944.0

Sample Code	Core Slice (cm)	Depth (cm)	Weight (g)	HCB (µg/kg)	CON 28 (µg/kg)	HEP (µg/kg)	CON 52 (µg/kg)	ALDRIN (µg/kg)	CON 101 (µg/kg)	pp-DDE (µg/kg)	Con 118 (µg/kg)	op-DDT (µg/kg)	CON 153 (µg/kg)	CON 138 (µg/kg)	CON 180 (µg/kg)	Σ ICES 7 (µg/kg)	Total Arochlor (µg/kg as 1254)
S31012A	0-3	1.5	33.1	1.2	2.0	1.3	2.0	0.0	3.9	3.2	3.0	0.0	3.4	4.3	2.1	20.7	77.3
S31012B	3-6	4.5	57.5	1.5	2.6	1.7	2.8	0.0	5.0	4.8	3.8	2.4	5.5	6.4	3.3	29.4	106.2
S31012C	6-9	7.5	69.8	1.8	3.6	2.9	4.2	0.0	7.9	4.6	4.9	2.8	7.8	9.6	5.0	43.0	151.2
S31012D	9-12	10.5	83.3	1.8	4.1	6.2	5.0	0.0	8.0	5.6	5.1	3.1	8.2	9.6	5.5	45.6	165.1
S31012E	12-15	13.5	87.2	2.6	7.1	3.6	5.8	0.0	14.2	8.3	9.4	3.9	13.5	17.0	8.9	76.0	181.2
S31012F	15-18	16.5	82.8	4.3	13.0	1.4	15.9	0.2	25.5	13.2	16.9	6.7	21.8	26.5	15.0	134.6	305.4
S31012G	18-21	19.5	86.3	6.9	9.9	7.5	14.3	0.0	24.4	14.6	14.5	7.0	19.2	23.3	11.9	117.6	271.1
S31012H	21-24	22.5	66.2	4.8	10.3	8.0	14.9	0.0	26.4	14.0	15.6	7.8	18.3	22.7	10.5	118.9	269.4
S31012I	24-27	25.5	126.7	8.8	5.1	9.6	9.7	0.0	24.2	17.5	14.7	9.2	15.9	20.0	8.1	97.6	231.7
S31012J	27-30	28.5	76.0	8.3	1.5	9.4	6.6	0.1	24.7	21.1	16.2	12.7	13.3	19.9	8.0	90.2	225.1
S31012K	30-33	31.5	85.7	3.6	1.0	8.8	6.8	0.2	23.8	23.2	15.6	12.7	13.0	18.3	8.1	86.6	212.4
S31012L	33-36	34.5	94.2	4.6	1.0	10.5	7.6	0.2	15.4	25.8	18.8	15.8	12.2	17.2	7.2	79.4	212.0
S31012M	36-39	37.5	78.3	4.8	0.1	7.6	5.1	0.1	14.8	26.7	15.2	12.1	10.5	16.4	6.2	68.3	187.3
S31012N	39-42	40.5	85.5	4.5	0.0	8.1	3.6	0.1	10.9	30.9	11.8	11.9	8.7	14.1	6.4	55.6	149.4
S31012O	42-45	43.5	80.2	6.2	0.8	11.0	4.2	0.0	7.7	23.2	8.0	5.8	7.4	9.2	4.7	42.0	100.4
S31012P	45-48	46.5	80.8	4.3	0.9	9.1	3.7	0.0	5.6	18.5	5.8	6.0	4.4	7.8	5.4	33.6	73.3
S31012Q	48-51	49.5	83.0	5.9	0.6	11.9	4.0	0.1	7.0	39.1	5.9	8.4	4.4	8.4	3.7	34.0	78.9
S31012R	51-54	52.5	90.0	4.1	0.4	10.2	2.9	0.0	4.6	31.6	3.7	1.5	2.6	2.9	2.3	19.3	41.2
S31012S	54-57	55.5	123.2	3.1	0.2	9.1	1.8	0.0	3.3	25.9	2.9	3.6	1.6	1.9	1.3	12.9	28.9
S31012T	57-60	58.5	72.9	4.5	0.1	11.2	2.2	0.0	4.3	50.9	3.4	6.6	2.0	2.3	1.3	15.7	36.1
S31002U	60-63	61.5	78.2	3.3	0.1	11.0	1.8	0.2	4.3	59.7	3.5	7.7	2.0	2.1	1.2	15.0	36.1
S31012V	63-66	64.5	84.9	1.7	0.0	9.3	1.3	0.0	2.8	35.3	2.4	4.2	1.1	1.6	1.0	10.2	25.6
S31012W	66-69	67.5	89.9	1.7	0.0	9.0	1.3	0.0	3.0	34.1	2.5	5.4	1.3	1.5	0.9	10.6	27.1
S31012X	69-72	70.5	125.8	1.6	0.0	6.7	0.8	0.1	1.9	31.2	1.5	4.0	0.6	0.9	0.5	6.2	17.7
S31012Y	72-75	73.5															
S31012Z	75-78	76.5															
S31012A1	78-81	79.5															
S31012B1	81-84	82.5															
S31012C1	84-87	85.5															
S31012D1	87-90	88.5															

Ince Core 2

Total Arochlor (µg/kg as 1:1:1)	A-HCH (µg/kg)	B-HCH (µg/kg)	G-HCH (µg/kg)	H/E (µg/kg)	DIELDRIN (µg/kg)	op-DDD (µg/kg)	ENDRIN (µg/kg)	pp-DDD (µg/kg)	op-DDT (µg/kg)	pp-DDT (µg/kg)	ΣDDT (µg/kg)	ΣHCH (µg/kg)	Am-241 Bq/kg	±2 Sigma Bq/kg	Cs-137 Bq/kg	Decay corrected Cs-137 Bq/kg
74.3	0.4	0.7	1.7	0.0	0.3	6.8	0.1	10.1	1.5	1.8	23.4	2.8	212.6	17.2	903.4	955.6
103.2	0.4	0.8	1.4	0.0	0.0	6.8	0.2	9.4	1.7	1.2	26.3	2.6	313.7	22.0	1667.6	1973.6
148.3	0.4	0.5	1.2	0.0	0.0	9.5	0.4	12.4	0.0	2.7	32.0	2.0	353.3	28.9	2336.3	3093.7
162.1	0.4	0.6	0.8	0.4	0.3	13.3	0.5	15.6	2.4	2.8	42.9	1.8	323.0	23.4	2459.6	3644.1
281.2	2.0	0.0	2.9	2.6	2.0	15.4	0.1	18.2	5.1	5.4	56.3	4.9	284.0	20.3	1774.7	2941.9
522.9	2.2	0.0	2.7	3.2	2.2	23.0	1.5	27.5	3.4	6.8	80.6	4.9	128.9	11.8	633.6	1175.2
435.4	2.2	0.0	3.2	2.7	2.2	23.9	0.3	28.5	6.3	7.7	88.1	5.4	29.7	4.3	130.8	271.4
451.7	1.7	0.0	2.8	2.3	0.0	23.5	0.1	33.3	5.5	7.3	91.5	4.5	8.3	3.8	85.9	199.5
337.5	2.3	2.5	3.3	2.8	2.1	33.1	2.6	59.2	6.4	7.7	133.1	8.1	5.4	4.0	65.0	168.9
311.8	2.3	2.7	3.6	3.0	2.1	43.9	4.0	79.8	6.9	10.4	175.0	8.7				
299.8	2.3	4.1	3.2	2.0	2.2	59.9	3.8	110.5	5.5	6.0	217.9	9.7	2.4	1.9	63.9	207.8
296.3	2.4	2.4	3.3	2.5	2.4	85.1	2.1	127.4	9.4	11.6	275.2	8.1				
244.8	3.1	4.4	5.2	2.2	1.7	85.6	2.7	134.9	8.0	11.0	278.2	12.7	**1.7**		63.2	257.3
198.9	2.6	3.2	3.5	0.0	2.5	107.2	6.2	150.7	10.2	18.4	329.2	9.3				
134.9	2.5	3.0	1.7		3.0	120.4	8.9	162.5	12.4	18.9	343.2	7.2	2.0	1.9	33.2	169.2
111.5	1.6	2.0	1.3	0.6	0.6	79.3	5.0	99.5	4.8	7.8	215.9	4.9				
104.1	2.2	6.6	1.6	0.2	0.4	102.5	5.8	145.3	5.3	12.6	313.1	10.4				
62.2	2.2	1.4	1.0	0.0	0.2	65.4	2.5	88.3	4.7	11.7	203.3	4.6	**1.5**		8.4	60.0
43.3	2.4	4.0	1.5	0.0	0.7	90.5	7.7	120.8	6.3	12.5	259.6	7.9				
50.0	2.7	8.2	1.9	0.7	0.0	119.4	8.7	175.1	6.3	19.3	377.5	12.8				
48.4	3.6	8.8	2.6	0.9	0.0	142.4	2.8	195.0	1.4	22.2	428.5	15.0				
33.2	4.0	11.8	1.7	0.8	0.2	194.6	5.8	268.2	10.7	24.8	537.8	17.5				
34.4	2.6	11.0	1.5	1.1	0.0	132.2	4.8	172.6	4.5	15.9	364.6	15.1				
21.9	2.8	12.3	1.9	0.6	0.0	133.8	8.2	187.4	12.5	25.5	394.4	17.0				

Ince Core 2

±2 Sigma Bq/kg	Pu-238 Bq/kg	Decay corrected Pu-238 Bq/kg	±2 Sigma Bq/kg	Pu-239+240 Bq/kg	±2 Sigma Bq/kg	Arsenic (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Original Dating Scheme (Murdock)	Time Signals	Final Dates by interpolation
49.1	24.0	24.5	0.7	127.2	1.5	30	125	84	2.8	150	400	1987.6	1990	1991.0
81.7	38.4	40.7	0.9	200.7	2.0	50	150	115	4.2	185	480	1982.8		1985.5
113.5	43.7	48.1	0.9	220.9	2.1	50	150	155	4.7	220	600	1978.0		1981.5
111.4	45.5	52.0	0.9	235.9	2.1	50	165	145	5.2	225	640	1973.2		1978.0
85.0	27.5	32.6	0.7	173.7	1.8	50	170	175	7.6	235	720	1968.4	1975	1975.5
34.1	10.6	13.1	0.5	117.6	1.6	60	175	190	6.5	290	760	1963.6		1972.5
7.6	1.7	2.2	0.2	37.1	0.9	80	160	170	5.2	270	760	1958.8	1970	1970.5
6.2	0.6	0.8	0.1	21.3	0.7	60	170	230	5.6	295	820	1954.0		1967.5
7.1	0.5	0.7	0.1	17.5	0.6	70	160	205	5.1	255	820	1949.2		1965.8
	0.2	0.3	0.1	7.9	0.4	80	160	190	5.1	255	820	1944.4		1963.5
3.2	0.2	0.3	0.1	8.4	0.4	60	165	295	5.6	295	880	1939.6		1961.5
	0.2	0.3	0.1	9.4	0.4	80	160	190	5.3	285	900	1934.8		1959.5
3.5						80	155	175	4.7	270	840	1930.0		1958.0
						70	160	200	5.2	280	820	1925.2		1956.3
2.4						70	165	245	5.2	265	840	1920.4		1954.3
						80	170	185	5.3	270	860	1915.6		1953.0
						70	170	180	4.7	285	860	1910.8	1952	1952.0
2.0						60	145	190	4.2	265	780	1906.0		1951.0
						60	165	170	4.6	255	720	1901.2		1950.0
						100	175	290	4.8	285	940	1896.4		1949.3
						110	185	235	5.3	315	1140	1891.6		1948.5
						90	205	230	5.4	330	940	1886.8		1947.8
						100	190	240	4.9	310	1000	1882.0		1947.3
						90	165	215	4.3	290	940	1877.2		1947.0
						90	165	240	4.8	265	980	1872.4		1946.8
						80	155	240	4.3	255	880	1867.6		1946.5
							155		4.7			1862.8		1946.0
							145		4.9			1858.0		1945.8
							130		4.8			1853.2		1945.5
							140		5.0			1848.4		1945.3
													1945	1945.0
														1944.8
														1944.5
														1944.0

Sample Code	Core Slice (cm)	Std Depth (cm)	Weight (g)	HCB (µg/kg)	CON 28 (µg/kg)	HEP (µg/kg)	CON 52 (µg/kg)	ALDRIN (µg/kg)	CON 101 (µg/kg)	pp-DDE (µg/kg)	CON 118 (µg/kg)	op-DDT (µg/kg)	CON 153 (µg/kg)	CON 138 (µg/kg)	CON 180 (µg/kg)	Σ ICES 7 (µg/kg)	Total Arochlor (µg/kg as 1254)
S31001A	0-3	1.5	25.6														
S31001B	3-6	4.5	87.8	2.1	2.5	2.1	2.6	1.8	4.6	2.3	3.5	0.0	5.4	5.5	3.5	27.6	96.7
S31001C	6-9	7.5	94.9	3.4	5.1	2.4	5.3	1.8	8.3	4.2	5.1	0.0	7.9	10.4	5.5	47.7	162.8
S31001D	9-12	10.5	104.6	3.5	7.2	5.3	8.9	2.2	11.7	5.2	7.3	0.0	10.5	12.8	7.2	65.5	227.4
S31001E	12-15	13.5	94.8	3.6	9.0	7.0	13.9	2.1	14.4	5.6	8.1	0.0	10.4	13.3	6.8	76.0	266.1
S31001F	15-18	16.5	120.0	5.5	9.1	19.2	23.2	3.5	29.5	13.1	18.8	11.1	20.1	26.0	9.7	136.4	512.0
S31001G	18-21	19.5	115.0	3.4	5.2	16.7	16.9	3.7	19.7	16.3	13.9	12.9	13.6	17.3	7.9	94.5	363.6
S31001H	21-24	22.5	102.2	7.6	2.2	16.6	6.3	4.7	10.2	28.0	8.8	9.9	7.9	12.9	5.3	53.7	216.8
S31001I	24-27	25.5	103.3	5.6	0.6	14.2	11.7	3.7	2.6	34.4	2.7	8.1	2.0	1.9	1.4	23.0	121.4
S31001J	27-30	28.5	110.3	19.8	0.0	25.9	4.4	2.3	2.2	10.2	1.5	15.9	1.0	5.6	0.7	15.3	92.7
S31001K	30-33	31.5	104.4	24.6	0.4	41.6	6.7	0.0	0.0	0.0	0.6	0.0	0.5	0.0	0.4	8.6	43.1
S31001L	33-36	34.5	105.3	25.6	0.5	0.8	1.4	0.0	0.4	0.4	0.3	0.0	0.4	0.3	0.3	3.6	18.1
S31001M	36-39	37.5	128.4	29.4	0.4	0.3	0.2	0.0	0.3	0.0	0.5	0.0	0.4	0.5	0.2	2.4	10.6
S31001N	39-42	40.5	97.7	21.0	0.4	0.4	0.2	0.0	0.0	0.0	0.4	0.0	0.3	0.4	0.2	1.9	8.8
S31001O	42-45	43.5	116.7	36.6	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.2	0.8
S31001P	45-48	46.5	115.2														
S31001Q	48-51	49.5	121.6														
S31001R	51-54	52.5	117.8														
S31001S	54-57	55.5	135.5														
S31001T	57-60	58.5	124.9														
S31001U	60-63	61.5	124.6														
S31001V	63-66	64.5	103.3														
S31001W	66-69	67.5	111.4														
S31001X	69-72	70.5	121.9														
S31001Y	72-75	73.5	125.0														
S31001Z	75-78	76.5	117.8														
S31001A1	78-81	79.5	143.4														
S31001B1	81-84	82.5	109.7														
S31001C1	84-87	85.5	115.5														
S31001D1	87-90	88.5	146.5														
S31001E1	90-93	91.5	118.8														
S31001F1	93-96	94.5	134.1														

Total Arochlor (µg/kg as 1:1:1)	A-HCH (µg/kg)	B-HCH (µg/kg)	G-HCH (µg/kg)	H/E (µg/kg)	DIELDRIN (µg/kg)	op-DDD (µg/kg)	ENDRIN (µg/kg)	pp-DDD (µg/kg)	op-DDT (µg/kg)	pp-DDT (µg/kg)	ΣDDT (µg/kg)	ΣHCH (µg/kg)	Am-241 Bq/kg	±2 Sigma Bq/kg	Cs-137 Bq/kg	Decay corrected Cs-137 Bq/kg
													189.6	18.3	801.2	850.3
66.6	0.8	0.0	1.4	0.0	7.5	13.7		14.3	2.9	8.1	41.2	2.2	236.9	18.3	#####	1442.5
105.6	1.2	0.0	2.6	0.7	13.6	16.4		17.9	4.4	11.8	54.7	3.8	278.0	23.9	#####	2391.1
135.5	1.0	3.5	2.8	0.6	15.4	22.5		24.6	5.3	12.9	70.5	7.3	268.5	22.9	#####	2366.0
143.9	1.3	0.9	0.9	0.7	14.2	18.4		17.3	4.0	11.6	56.8	3.1	147.2	13.1	902.9	1503.8
303.1	5.5	4.5	1.8	0.5	22.1	68.1		59.8	10.6	23.0	185.7	11.9	**4.0**		88.7	163.6
199.1	4.2	35.4	1.5	0.6	21.6	95.5		110.7	12.6	24.1	272.0	41.0	**2.2**		80.2	163.2
138.8	12.6	194.7	3.4	0.0	4.8	148.7		237.9	9.0	27.5	461.0	210.7				
39.4	19.8	163.2	3.7	0.3	0.6	189.5		286.9	10.8	35.4	565.1	186.8	**1.9**		4.3	10.5
39.2	85.5	48.7	6.8	0.3	0.4	112.7		121.5	8.3	25.8	294.3	141.1				
7.5	1.3	7.1	1.5	2.7		3.2		4.3	1.3	0.0	8.9	10.0	**2.0**		**1.3**	
5.6	0.3	1.1	1.5	0.0		0.0		0.0	0.0	0.0	0.4	2.9				
6.0	0.2	0.0	1.3	0.0		0.0		0.0	0.0	2.7	2.7	1.5	1.9	1.7	**1.1**	
5.2	0.0	0.0	1.1	0.0		0.0		0.0	0.5	0.0	0.5	1.1				
0.4	0.0	1.2	0.0	0.0		0.0		0.0	0.0	0.0	0.0	1.2	**1.8**		**1.1**	
													2.0		**2.4**	

±2 Sigma Bq/kg	Pu-238 Bq/kg	Decay corrected Pu-238 Bq/kg	±2 Sigma Bq/kg	Pu-239+240 Bq/kg	±2 Sigma Bq/kg	Plut ratio	Arsenic (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Original Dating Scheme (Murdock)	Time Signals	Final Dates by linear regr
46.2	23.1	23.6	0.8	121.9	1.9	0.19	30	125	84	2.8	215	440	1988.9	1990	1989.0
61.9	29.9	31.8	1.0	159.7	2.3	0.20	40	150	120	4.3	170	540	1985.5		1985.0
90.2	35.9	39.7	1.1	194.2	2.6	0.20	50	170	140	5.3	205	620	1982.1		1980.0
82.1	32.7	37.5	1.0	182.0	2.4	0.21	50	155	155	6.3	225	700	1978.6	1975	1975.0
45.9	15.1	17.9	0.7	100.1	1.9	0.18	50	165	185	6.3	295	900	1975.2	1970	1971.0
11.3	0.4	0.4	0.1	12.9	0.7	0.03	60	175	215	5.9	295	1060	1971.8		1966.0
6.9	0.4	0.5	0.1	11.5	0.6	0.04	70	180	260	5.5	335	1140	1968.4		1961.0
	0.2	0.2	0.1	5.3	0.4	0.05	70	180	440	5.7	430	1340	1965.0		1957.0
1.6	0.1	0.1	0.0	1.5	0.1	0.10	80	190	380	5.8	410	1360	1961.6	1952	1952.0
	0.1	0.2	0.0	0.1	0.0	2.14	140	180	400	5.6	550	1800	1958.1		1947.0
	0.1	0.2	0.0	0.2	0.1	1.00	140	200	530	6.2	570	1680	1954.7	1943	1943.0
	0.1	0.1	0.0	0.1	0.0	1.40	200	230	450	6.4	550	1500	1951.3		1938.0
							220	210	380	4.7	410	1620	1947.9		1933.0
							280	245	400	5.4	490	2150	1944.5		1929.0
							380	225	480	4.6	470	2550	1941.1		1924.0
							300	225	640	4.1	460	2600	1937.6		1919.0
							560	225	400	3.9	470	2200	1934.2		1915.0
							460	305	400	5.5	510	2250	1930.8		1910.0
							560	315	370	6.0	610	2100	1927.4		1905.0
							640	190	300	4.2	540	1640	1924.0		1901.0
							520	170	315	3.9	500	1420	1920.6		1896.0
							560	160	295	3.5	540	1120	1917.1		1891.0
							300	140	240	4.2	395	600	1913.7		1887.0
							190	110	215	2.2	305	360	1910.3		1882.0
							100	140	160	1.7	320	290	1906.9		1877.0
							70	160	145	0.8	310	280	1903.5		1873.0
							40	130	92	0.7	195	180	1900.0		1868.0
							25	60	76	0.6	145	150	1896.6		1863.0
							15	60	78	0.6	135	150	1893.2		1859.0
							20	45	58	0.3	110	140	1889.8		1854.0
							15	45	54	0.4	92	120	1886.4		1849.0
							15	40	56	0.2	94	120	1883.0		1845.0

Sample Code	Core Slice (cm)	Depth (cm)	Weight (g)	HCB (µg/kg)	CON 28 (µg/kg)	HEP (µg/kg)	CON 52 (µg/kg)	ALDRIN (µg/kg)	CON 101 (µg/kg)	pp-DDE (µg/kg)	CON 118 (µg/kg)	op-DDT (µg/kg)	CON 153 (µg/kg)	CON 138 (µg/kg)	CON 180 (µg/kg)	∑ ICES 7 (µg/kg)	Total Arochlor (µg/kg as 1254)
S31002A	0-3	1.5	63.3	1.6	2.2	1.3	3.0	0.0	5.2	4.7	3.8	0.0	5.0	5.6	2.6	27.4	104.1
S31002B	3-6	4.5	92.0	1.7	2.3	4.2	4.8	0.0	7.6	4.5	4.4	2.6	7.3	8.7	4.5	39.6	141.6
S31002C	6-9	7.5															
S31002D	9-12	10.5	75.1	4.8	20.4	8.8	26.2	8.4	34.5	17.9	18.4	12.9	22.4	30.0	16.6	168.5	531.9
S31002E	12-15	13.5	113.2	6.2	12.5	26.5	23.5	1.6	38.4	27.5	20.3	17.9	27.6	34.2	15.8	172.4	444.3
S31002F	15-18	16.5	103.7	2.1	6.2	26.8	14.5	0.9	34.2	45.7	26.1	22.4	21.1	30.5	14.6	147.3	291.5
S31002G	18-21	19.5	97.6	5.8	3.0	31.1	13.2	0.3	26.7	68.5	25.9	17.6	25.0	34.4	13.7	141.9	310.2
S31002H	21-24	22.5	113.1	5.0	0.5	22.1	4.2	0.4	7.3	70.2	6.2	3.0	4.8	4.9	3.8	31.7	87.0
S31002I	24-27	25.5	107.7	11.3	0.2	39.7	2.5	0.3	6.5	66.8	4.9	3.6	3.1	13.3	1.9	32.5	75.2
S31002J	27-30	28.5	100.6	20.6	0.0	89.0	2.9	0.2	6.6	1.9	1.6	0.0	1.0	21.8	1.1	34.8	73.1
S31002K	30-33	31.5	95.8	9.0	0.2	5.7	2.7	0.0	0.7	0.4	0.6	0.9	0.3	2.8	0.3	7.5	20.4
S31002L	33-36	34.5	121.6	18.9	0.1	0.4	0.3	0.0	0.6	0.4	0.6	0.0	0.3	0.5	0.2	2.5	7.3
S31002M	36-39	37.5	110.8	17.0	0.2	0.8	0.6	0.0	0.6	0.6	1.0	0.0	0.8	1.2	0.5	4.9	9.7
S31002N	39-42	40.5	119.8	22.3	0.2	0.2	0.0	0.1	0.0	0.1	0.2	0.0	0.2	0.2	0.1	0.8	1.3
S31002O	42-45	43.5	101.2	14.0	0.1	0.2	0.2	0.0	0.0	0.1	0.2	0.0	0.1	0.2	0.2	1.0	3.1
S31002P	45-48	46.5	112.2	11.2	1.9	0.8	0.0	0.3	0.3	0.2	0.2	0.0	0.2	0.4	0.2	3.1	2.0
S31002Q	48-51	49.5	104.7	15.6	0.0	0.4	0.0	0.0	0.2	0.1	0.3	0.0	0.1	0.4	0.3	1.3	2.4
S31002R	51-54	52.5	116.2	12.8	0.1	0.4	0.0	0.0	0.2	0.0	0.3	0.2	0.1	0.3	0.3	1.3	1.5
S31002S	54-57	55.5															
S31002T	57-60	58.5	117.1	8.9	0.1	0.5	0.0	0.0	0.2	0.0	0.3	0.0	0.1	0.4	0.2	1.3	1.9
S31002U	60-63	61.5	122.2	6.1	0.1	0.5	0.0	0.0	0.3	0.0	0.3	0.0	0.3	0.4	0.0	1.3	0.0
S31002V	63-66	64.5	123.8	2.5	0.3	0.3	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.2	0.0	0.8	3.5
S31002W	66-69	67.5	123.0	0.9	1.0	0.6	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0
S31002X	69-72	70.5	123.2	0.4	0.4	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0
S31002Y	72-75	73.5	125.8	0.3	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
S31002Z	75-78	76.5	122.9	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
S31002A1	78-81	79.5	130.6	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
S31002B1	81-84	82.5	127.2	0.2	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S31002C1	84-87	85.5	124.6	0.5	0.0	0.4	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0
S31002D1	87-90	88.5	133.2	0.2	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S31002E1	90-93	91.5	131.6	0.6	0.0	0.1	0.3	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0
S31002F1	93-96	94.5	153.1	0.8	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0
S31002G1	96-99	97.5	152.9	1.2	0.3	0.4	0.6	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.8	0.0
S31002H1	99-102	100.5	151.6	2.0	0.4	0.4	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	0.0

Total Arochlor (µg/kg as 1:1:1)	A-HCH (µg/kg)	B-HCH (µg/kg)	G-HCH (µg/kg)	H/E (µg/kg)	DIELDRIN (µg/kg)	op-DDD (µg/kg)	ENDRIN (µg/kg)	pp-DDD (µg/kg)	op-DDT (µg/kg)	pp-DDT (µg/kg)	ΣDDT (µg/kg)	ΣHCH (µg/kg)	Am-241 Bq/kg	± 2 Sigma Bq/kg	Cs-137 Bq/kg	Decay corrected Cs-137 Bq/kg
68.2	0.6	2.2	2.3	0.6	0.0	10.9	0.0	11.1	1.0	2.9	30.6	5.2	207.9	18.7	919.2	1026.3
94.4	0.9	1.4	1.7	0.0	0.0	10.8	0.0	11.6	0.0	2.9	32.5	4.0	289.1	22.7	1730.6	2186.2
													280.6	24.6	1757.1	2497.5
330.7	0.9	5.7	1.9	1.0	0.0	28.6	3.8	37.5	0.0	11.0	107.9	8.6	92.6	5.3	568.5	904.4
325.8	1.7	8.0	1.2	1.2	0.3	49.6	5.5	56.7	6.9	13.3	171.9	10.9	8.1	3.4	90.2	159.8
219.1	1.2	22.2	0.8	0.8	0.5	79.9	4.0	103.4	10.7	22.9	285.0	24.2	**3.7**		64.1	126.0
270.9	11.5	129.6	2.8	0.5	1.1	127.4	4.7	194.3	8.8	30.3	447.0	143.8	**2.0**		39.5	85.7
61.1	12.1	118.8	2.7	0.2	0.0	103.8	2.6	146.4	5.1	20.5	349.0	133.6				
66.4	19.9	165.6	5.4	0.3	0.0	155.4	5.0	211.8	7.1	23.9	468.7	190.9	**2.1**		**1.5**	
67.3	6.1	58.7	1.4	0.5	0.3	7.1	5.3	7.6	0.0	0.0	16.6	66.2				
10.9	2.3	20.6	1.3	0.6	0.0	0.9	9.9	3.1	0.0	0.0	5.4	24.2	**1.9**		**1.3**	
6.3	1.3	14.4	0.3	0.5	0.2	0.6	8.5	9.5	0.0	0.0	10.6	16.0				
8.6	1.8	19.3	1.1	1.5	0.3	1.0	11.2	12.6	6.4	0.0	20.7	22.3				
0.9	1.6	12.7	2.5	0.5	0.0	1.6	4.7	7.0	4.6	0.0	13.3	16.8				
0.9	1.6	10.6	2.5	0.6	0.0	1.1	3.9	1.5	0.0	0.0	2.7	14.7				
1.6	1.9	10.5	2.1	0.0	0.0	0.6	6.9	2.3	0.0	0.0	3.1	14.4				
1.7	1.5	8.4	2.2	0.3	0.0	0.8	7.3	7.4	3.6	0.0	11.9	12.1				
0.6	1.5	6.9	2.2	0.5	0.0	1.3	6.1	7.0	0.0	0.0	8.4	10.6				
0.8	1.7	4.2	3.0	0.4	0.0	1.0	6.0	0.8	0.0	0.0	1.9	9.0				
0.8	0.9	2.6	1.6	0.8	0.0	0.7	6.0	0.0	0.0	0.0	0.7	5.1				
1.1	0.0	0.7	1.7	0.6	0.0	0.8	3.6	3.0	0.0	0.0	3.8	2.4				
0.2	0.5	0.8	1.3	0.2	0.1	0.2	2.3	1.6	0.0	0.0	1.8	2.5				
0.1	0.0	0.8	1.8	0.6	0.0	0.6	3.5	0.0	0.0	0.7	1.3	2.6				
0.0	0.2	0.9	1.2	0.4	0.0	0.3	2.5	0.0	0.0	0.0	0.3	2.3				
0.0	2.3	1.2	0.8	0.0	0.0	0.4	5.0	0.0	0.0	0.0	0.4	4.2				
0.0	1.2	1.6	1.3	0.5	0.0	0.7	1.1	0.4	0.0	0.0	1.1	4.1				
0.0	0.3	0.8	1.0	0.3	0.0	0.0	1.0	0.0	0.0	0.0	0.0	2.1				
0.0	0.2	0.6	0.7	0.0	0.0	0.5	2.8	0.5	0.0	0.0	1.0	1.5				
0.0	0.5	1.0	0.6	0.0	0.0	0.5	1.8	0.4	0.0	0.0	1.0	2.0				
0.0	0.1	0.5	0.7	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.1	1.4				
0.0	0.8	0.8	2.1	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	3.7				
0.0	0.3	0.6	1.3	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.1	2.2				
0.0	0.5	0.8	2.1	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	3.3				

±2 Sigma Bq/kg	Pu-238 Bq/kg	Decay corrected Pu-238 Bq/kg	±2 Sigma Bq/kg	Pu-239+240 Bq/kg	±2 Sigma Bq/kg		Arsenic (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Original Dating Scheme (Murdock)	Time Signals	Final Dates by linear regr
48.4	24.4	25.3	0.9	129.6	2.0	0.20	40	140	98	3.2	160	480	1988.7	1990	1987.0
77.9	34.3	37.2	1.0	180.1	2.3	0.21	60	150	140	5.0	205	600	1984.8		1982.0
82.2	27.8	31.3	0.9	161.2	2.2	0.19	70	160	190	6.4	265	760	1981.0	1975	1977.0
21.3	7.5	8.8	0.5	69.3	1.4	0.13	70	160	215	6.4	310	960	1977.1	1970	1972.0
6.1	0.6	0.7	0.1	16.0	0.8	0.04	80	175	220	6.1	315	1100	1973.3		1967.0
6.3	0.2	0.2	0.1	8.5	0.5	0.02	80	175	255	6.2	295	1100	1969.4		1962.0
2.9	0.2	0.3	0.1	6.0	0.5	0.04	90	185	470	5.9	410	1280	1965.5		1957.0
	0.1	0.2	0.1	2.8	0.3	0.07	110	185	385	5.5	375	1260	1961.7	1952	1952.0
	0.1	0.1	0.0	0.2	0.1	0.54	90	195	420	6.0	500	1540	1957.8	1945	1947.0
				0.1	0.0	0.00	130	200	500	6.7	600	1580	1954.0		1942.0
				0.0	0.0	0.00	170	250	520	7.5	500	1460	1950.1		1937.0
	0.1	0.2	0.0	0.1	0.1	1.15	240	195	350	4.3	430	1700	1946.3		1932.0
							280	250	450	5.7	480	2100	1942.4		1928.0
							520	225	580	4.1	480	2700	1938.6		1923.0
							480	230	480	3.8	450	2400	1934.7		1918.0
							520	265	410	4.5	470	2250	1930.8		1913.0
							720	330	400	6.0	580	2150	1927.0		1908.0
							700	280	360	5.5	560	1960	1923.1		1903.0
							720	185	380	4.5	480	1780	1919.3		1900.0
							580	165	285	3.7	480	1380	1915.4		1895.0
							460	165	370	4.3	620	1300	1911.6		1890.0
							280	145	215	3.0	360	680	1907.7		1885.0
							190	115	180	2.6	280	520	1903.9		1882.0
							140	135	185	2.2	315	420	1900.0		1879.0
							100	160	125	1.1	285	310	1896.2		1874.0
							60	140	120	1.0	215	260	1892.3		1869.0
							40	90	105	0.8	205	240	1888.4		1865.0
							30	95	84	0.8	165	160	1884.6		1860.0
							30	45	64	0.4	110	140	1880.7		1855.0
							25	45	68	0.4	92	160	1876.9		1844.0
							30	45	54	0.3	84	130	1873.0		1839.0
							20	40	44	0.2	60	120	1869.2		1834.0
							20	40	38	0.2	58	110	1865.3		1829.0
							20	40	32	0.2	50	100	1861.5		1823.0

%Loss on ignition

Depth Widnes	%LOI Widnes1	%LOI Widnes2	Depth Banks	%LOI Banks1	%LOI Banks2	Depth Ince1	%LOI Ince1	Depth Ince2	%LOI Ince2
0		20.15	0	11.34	13.18	0	15.63	1.5	20.03
3	15.4	14.63	3	13.27	9.84	3	16.75	4.5	15.54
6	16.23		6	12.75		6	11.69	7.5	13.62
9	15.78	16.14	9	9.92	7.77	9	11.7	10.5	11.12
12	14.52	13.37	12	9.55	6.8	12	14.12	13.5	12.1
15	12.87	12.14	15	10.02	8.32	15	12.86	16.5	14.03
18	13.44	14.35	18	9.36	6.79	18	11.95	19.5	13.37
21	14.26	12.06	21	9.41	7.51	21	10.69	22.5	11.44
24	14.28	15.88	24	8.94	6.39	24	8.21	25.5	9.5
27	14.89	16.9	27	5.89	6.43	27	7.49	28.5	9.3
30	16.05	16.59	30	5.07	5.79	30	9.87	31.5	9.06
33	14.99	14.36	33	4.8	5.66	33	10.38	34.5	10.23
36	12.37	14.72	36	5.19	5.88	36	10.22	37.5	9.75
39	14.42	14.17	39	7.06	5	39	9.56	40.5	8.91
42	12.57	14.21	42	6.47	5.12	42	8.76	43.5	10.06
45	12.59	14.6	45	4.8	6.31	45	9.42	46.5	9.92
48	12.15	13.73	48	4.47	5.49	48	10.03	49.5	10.8
51	13.42	13.01	51	5.39	5.15	51	8.39	52.5	8.89
54	13.47		54	6.47		54	9.66	55.5	8.62
57	11.65	12.19	57	3.23	4.34	57	9.04	58.5	8.86
60	12.84	13.37	60	5.75	2.44	60	6.95	61.5	9.87
63	12.17	12.19	63	7.16	4.91	63	9.87	64.5	9.55
66	10.96	6.69	66	7.55	4.96	66	8	67.5	9.57
69	14.34	10.83	69	5.93	4.36	69	7.63	70.5	7.68
72	10.1	10.79	72	5.64	4.71	72	6.11		
75	9.05	10.14	75	6.07	4.41	75	7.02		
78	8.92	8.59	78	3.6	4.44	78	7.69		
81	7.1	7.98	81	3.72	4.32	81	7.07		
84	7.5	7.81	84	5.63	4.68	84	5.23		
87	7.44	7.4	87	2.55	2.44	87	6.07		
90	7.18	7.8	90	1.76	0.9	90	6.73		
93	6.89	6.26	93	1.67	1.03	93	7.01		
96		6.27	96	1.46	1.22	96	6.69		
99		6.18	99	1.46	0.92	99	6.74		